Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information for:

Simple Inexpensive Boron Electrophiles for Direct Arene Borylation

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Contents of Supporting Information:

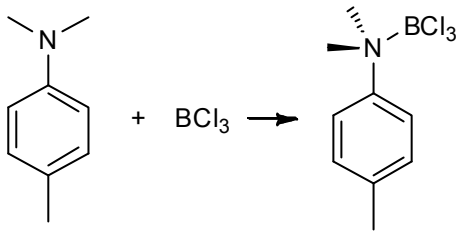
General Considerations: All manipulations were performed using standard Schlenk techniques or in an argon-filled MBraun glovebox (O_2 levels below 0.5 ppm). Glassware was dried in a hot oven overnight and heated under vacuum before use. Solvents and Et_3N were distilled from Na/benzophenone, CaH_2 or P_2O_5 and degassed prior to use. TIPS protected N-heterocycles were made by published procedures from the parent heterocycle. All other materials were purchased from commercial vendors and used as received. NMR spectra were recorded with a Bruker AV-400 spectrometer (400 MHz ^{1}H; 100 MHz ^{13}C; 128 MHz ^{11}B; 162 MHz ^{31}P; 62 MHz, ^{27}Al 104.3 MHz). ^{1}H NMR chemical shifts are reported in ppm relative to protio impurities in the deuterated solvents and ^{13}C NMR using the centre line of CD_2Cl_2 (or $CDCl_3$ as appropriate) as internal standard. ^{11}B NMR spectra were referenced to external BF_3:Et_2O, and ^{27}Al to $Al(NO_3)_2$ in D_2O ($Al(H_2O)_6^{3+}$). Unless otherwise stated all NMR are recorded at 293 K. Elemental analysis of air sensitive compounds were performed by London Metropolitan University service. Broad features in the ^{11}B and ^{27}Al NMR spectra are due to boron materials present in the spectrometer probe/NMR tube glass. Resonances for the carbon directly bonded to boron are not observed in the $^{13}C\{^{1}H\}$ NMR spectra.

BCl_3 purchased as a 1M solution in CH_2Cl_2 or heptanes was found to be of variable molarity. Therefore an excess of reagents can be used to ensure sufficient borylating agent is present for full borylation.

For large scale where this is not economical and reactions where product distribution was sensitive to stoichiometry the molarity of BCl_3 solutions was approximately quantified by titration with PPh_3 (using ^{11}B and $^{31}P\{^{1}H\}$ NMR spectroscopy).

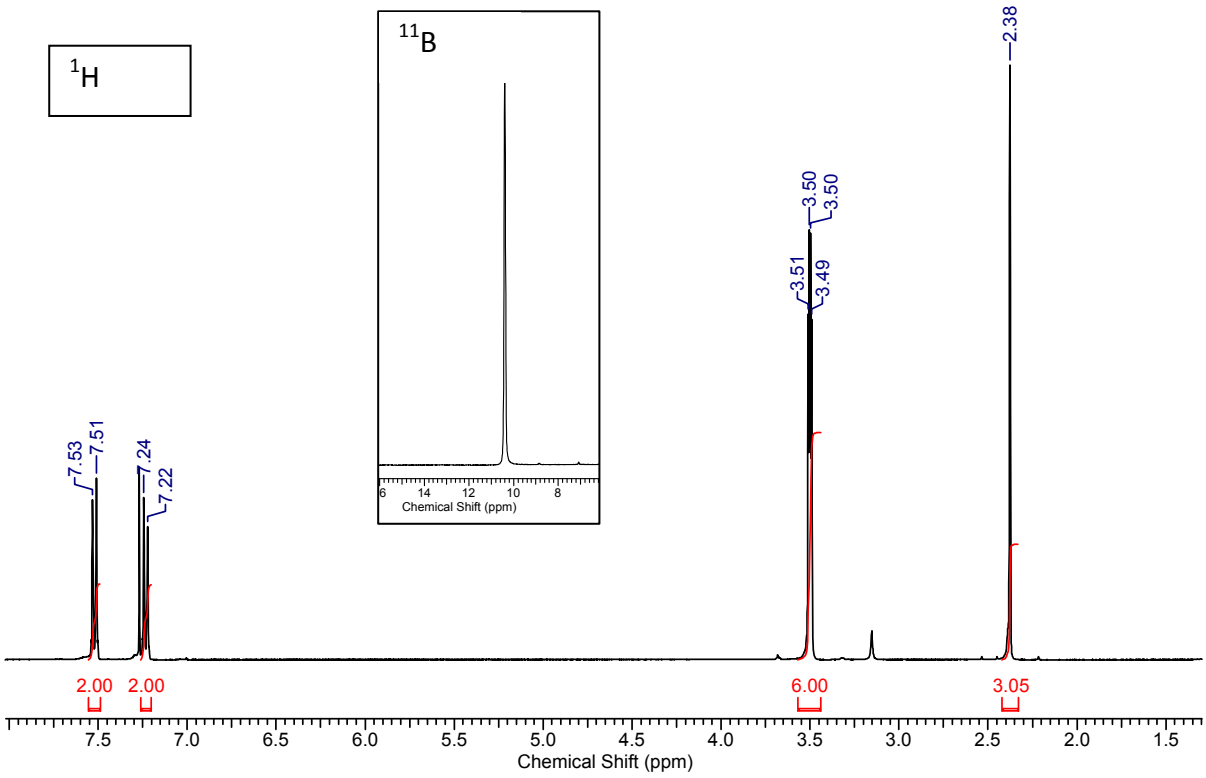
Alternatively equimolar Me_2NTol and BCl_3 (in heptanes) combined in hexanes results in precipitation of the adduct $(Me_2NTol)BCl_3$ as a colourless solid which can then be readily isolated and used to obtain exact stoichiometries. Furthermore $(Me_2NTol)BCl_3$ can be handled for short periods in air.

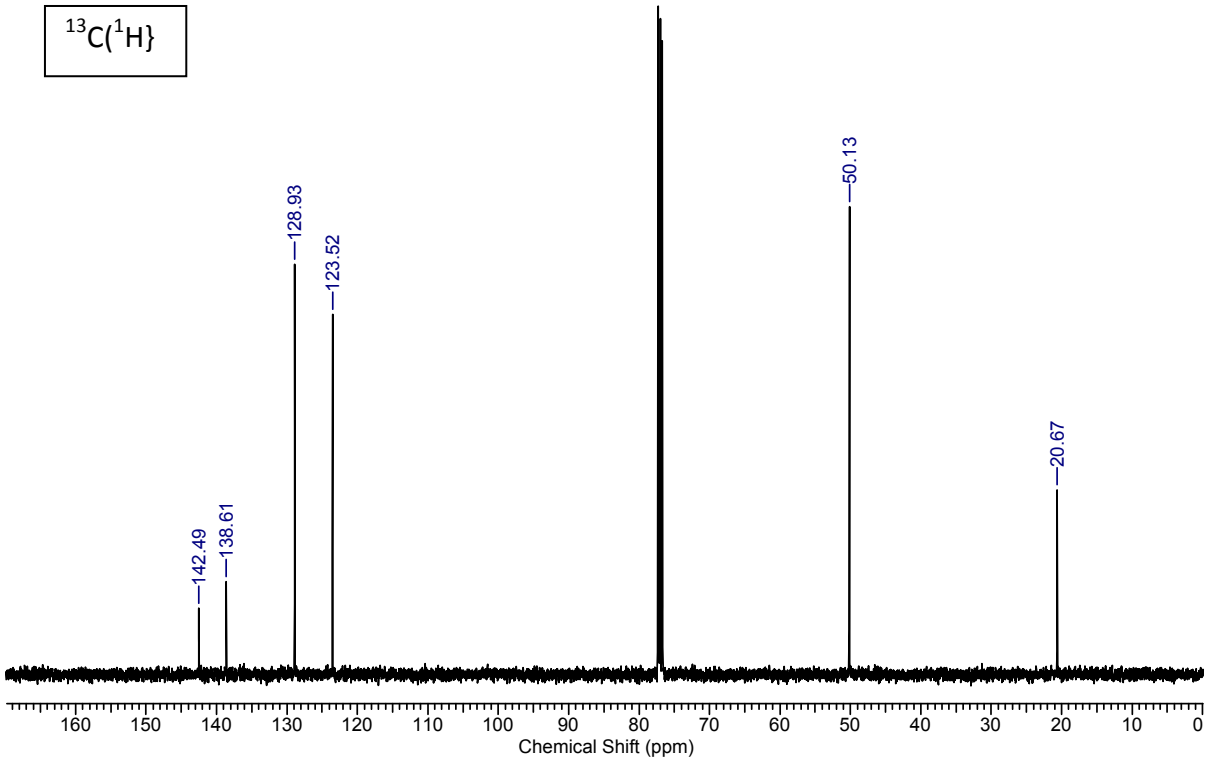
Synthesis of ($Me_2NTol)BCl_3$ adduct:



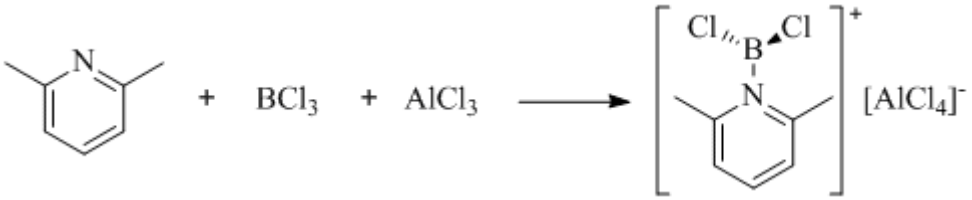
In an oven dried Schlenk tube under inert atmosphere Me_2NTol (3 ml, 20.8 mmol, 1 equiv.) was dissolved in dry pentane (15 ml). To the solution cooled at 0 °C, a solution of BCl_3 (1M in heptanes, 16 ml, 16 mmol, 0.77 eqiv.) was added dropwise to form a white solid, and then warmed at room temperature. After stirring for 1 hour the solution was removed by filter cannula and the solid washed with dry pentane (2 x 50 ml). The white solid was dried under vacuum to give the desired product (3.9 g, 97%) which is stored in the glovebox.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (2 H, d, *J* = 8.8 Hz), 7.23 (2 H, d, *J* = 8.6 Hz), 3.50 (6 H, q), 2.38 (3H, s). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 142.5, 138.6 128.9, 123.5, 50.1, 20.7. ^{11}B NMR (128 MHz, $CDCl_3$) δ 10.4





Synthesis [Cl_2B(2,6-lutidine)][$AlCl_4$], 1:



a) In an oven dried Schlenk fitted with a J. Young's tap 2,6-lutidine (93 µl, 0.80 mmol, 1 equiv.) was dissolved in CH_2Cl_2 (1 ml) and BCl_3 (0.8 M in CH_2Cl_2, 1 ml, 0.80 mmol, 1 equiv.) was slowly added. Then to this mixture $AlCl_3$ (106 mg, 0.80 mmol, 1 equiv.) was added and stirred until all $AlCl_3$ was dissolved. The resulting mixture was layered with pentane. Colourless crystals and brown oil were formed after diffusion was complete. The brown oil and solution were removed by cannula and the crystals were washed with pentane (0.5 ml). The crystals were dried under vacuum yielding [Cl_2B(2,6-lutidine)][$AlCl_4$] (115 mg, 0.32 mmol, 40 %) as colourless solid.

^{1}H NMR (CH_2Cl_2/CD_2Cl_2) δ: 8.50 (t, *J* = 8.1 Hz, 1 H), 7.88 (d, *J* = 7.8 Hz, 2 H), 2.93 (s, 6 H).

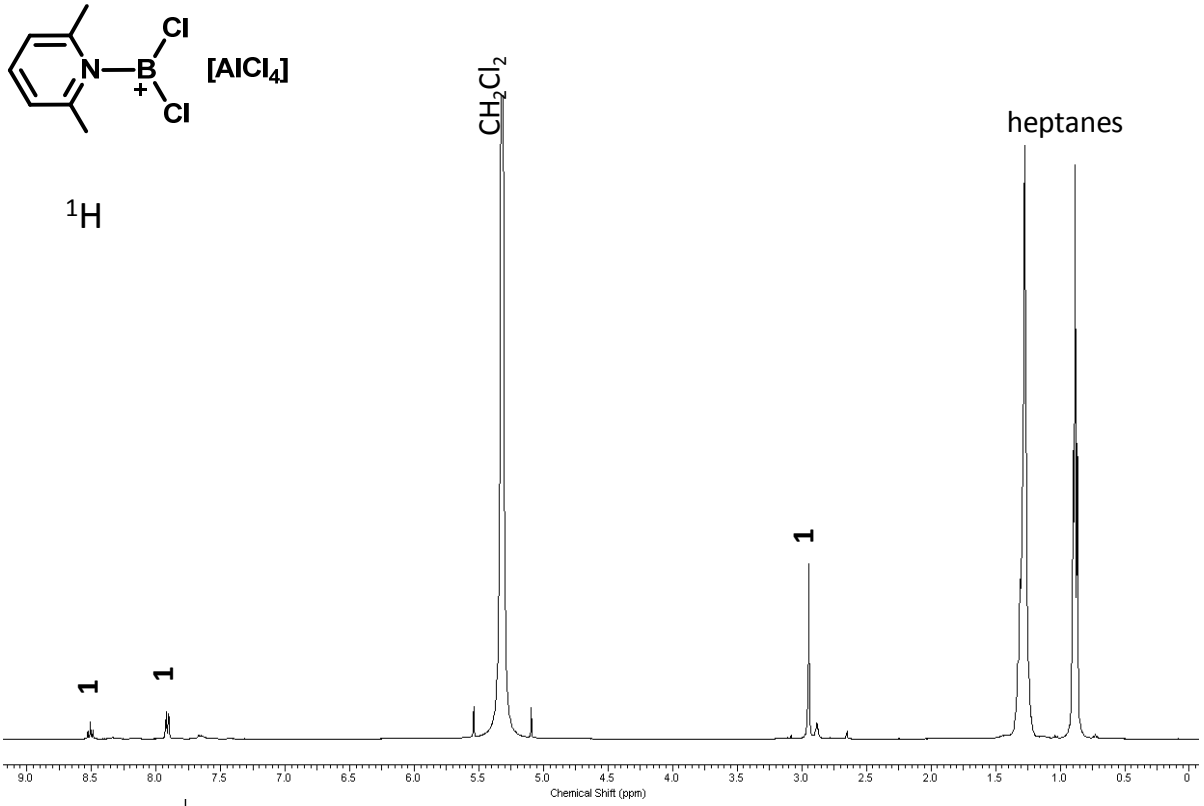
^{13}C{^{1}H} NMR (CH_2Cl_2/CD_2Cl_2) δ: 153.0, 149.0, 127.8, 22.5.

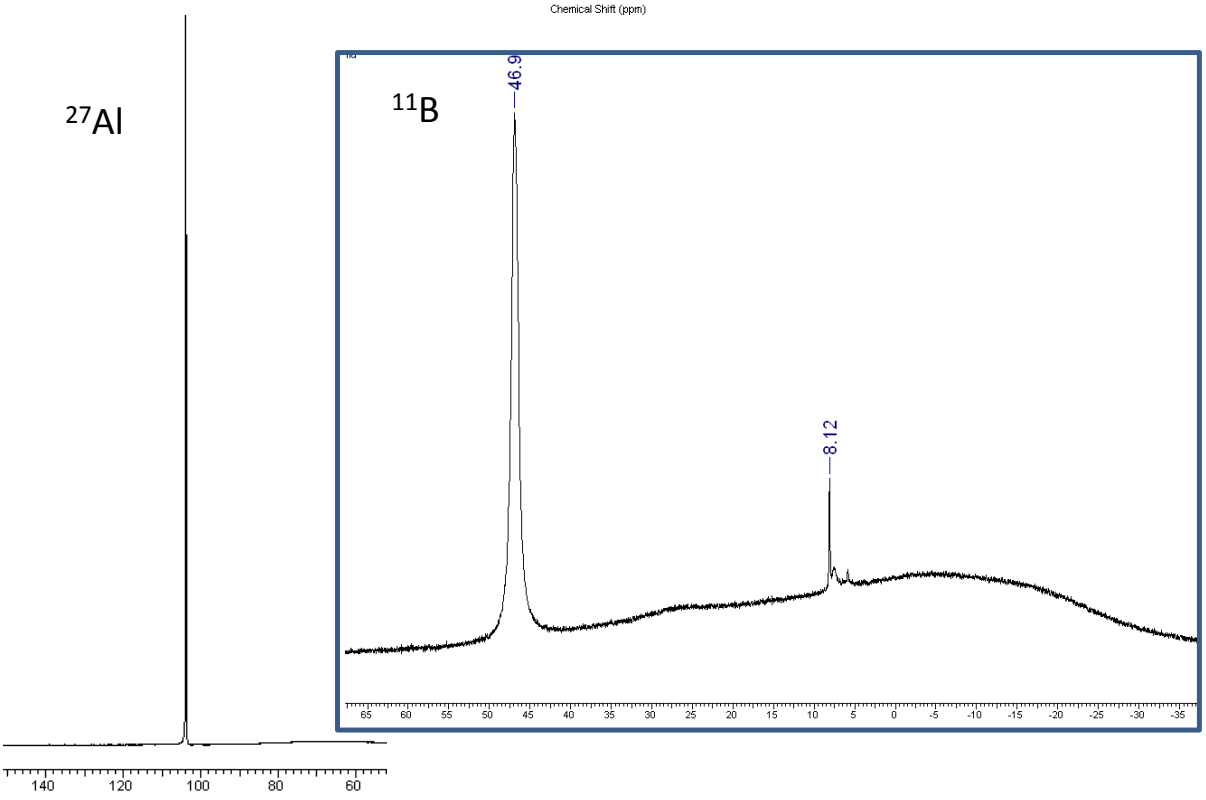
^{11}B NMR (CH_2Cl_2/CD_2Cl_2) δ: 46.9 (br s, pwhh = 126 Hz).

Anal. Calc. for $C_7H_9AlBCl_6N$: C 23.51; H 2.54; N 3.86. Found: C 23.42; H 2.64; N 3.86.

b) In an oven dried Schlenk fitted with a J. Young's tap 2,6-lutidine (58 µl, 0.50 mmol, 1 equiv.) was dissolved in *ortho*-dichlorobenzene (1 ml) and BCl_3 (1.0 M in heptane, 0.5 ml, 0.50 mmol, 1 equiv.) was slowly added. Then to this mixture $AlCl_3$ (67 mg, 0.50 mmol, 1 equiv.) was added and then heated at 90 ºC for 10 min. On slow cooling single crystals suitable for X-ray were grown.

Whilst the isolated yields of crystalline **1** are only moderate at best, the in-situ NMR spectra clearly show the only major species formed on combination of equimolar BCl_3 (1M in CH_2Cl_2 or in heptanes) /$AlCl_3$/2,6-lutidine is **1** (> 95 % by ^{11}B). Overleaf are representative NMR spectra (in a mix of CH_2Cl_2 and CD_2Cl_2) from the combination of equimolar BCl_3 (1M in heptanes)/$AlCl_3$/2,6-lutidine.

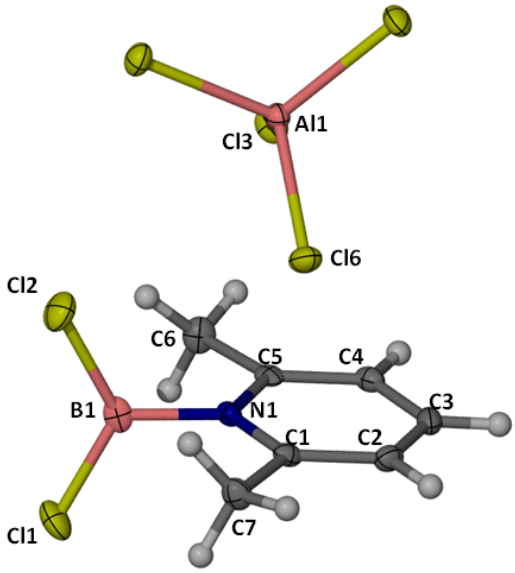

Cl
N
B
+
Cl
[AlCl4]
1H
CH2Cl2
heptanes
1
1
1
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

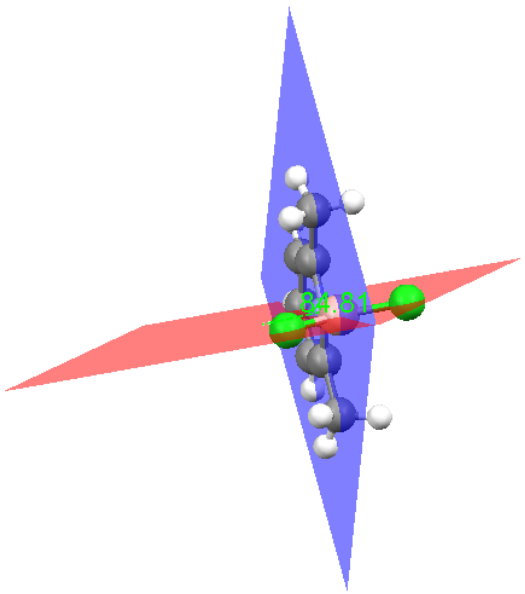

27Al
140
120
100
80
60
11B
46.9
8.12
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35

Crystallographic Details of Compound **1**

$C_7H_9B_1Al_1Cl_6N_1$,M = 357.64, monoclinic, a = 7.345(5), b = 13.689(5), c = 14.699(5) Å, β = 99.057(5)°, V = 1459.5(12)Å^3, T = 100(2) K , space group P.21/n, Z = 4, R_{int} = 0.0436 (for 8580 measured reflections), R_1 = 0.0288 [for 1937 unique reflections with >2s(I)], wR^2 = 0.0599 (for all 2576 unique reflections).

Below, left the molecular structure of **1**, thermal ellipsoids at 50% probability. The closest anion-cation contact is B1-Cl6 at 3.809 Å. Right the orthogonal arrangement with an interplane angle of 84.81° (green = Cl, pink = boron, dark grey = carbon, blue = nitrogen)





Selected Bond lengths (Å) and angles (°):

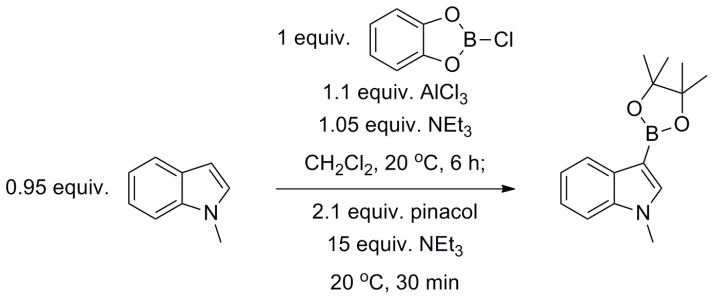
Cl6 Al1 2.1311(12)
Cl5 Al1 2.1331(12)
Cl4 Al1 2.1366(14)
Cl3 Al1 2.1371(13)
Cl1 B1 1.709(3)
Cl2 B1 1.715(3)
C5 C4 1.368(3)
C5 N1 1.374(3)
C5 C6 1.493(3)
C4 C3 1.368(3)
C7 C1 1.491(3)
C2 C1 1.371(3)
C2 C3 1.383(3)
N1 C1 1.367(3)
N1 B1 1.508(3)

C4 C5 N1 118.4(2) . . ?
C4 C5 C6 123.7(2) . . ?
N1 C5 C6 117.9(2) . . ?
C3 C4 C5 120.6(2) . . ?
C1 C2 C3 119.5(2) . . ?
C4 C3 C2 120.4(2) . . ?
C1 N1 C5 122.0(2) . . ?
C1 N1 B1 118.46(19) . . ?
C5 N1 B1 119.5(2) . . ?
N1 C1 C2 119.1(2) . . ?
N1 C1 C7 117.8(2) . . ?
C2 C1 C7 123.1(2) . . ?
N1 B1 Cl1 117.51(19) . . ?

N1 B1 Cl2 119.6(2) . . ?
Cl1 B1 Cl2 122.89(17)

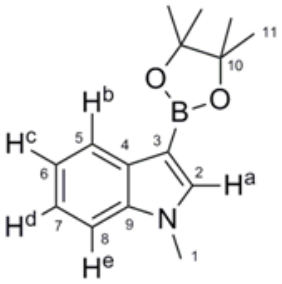
Large Scale Borylations

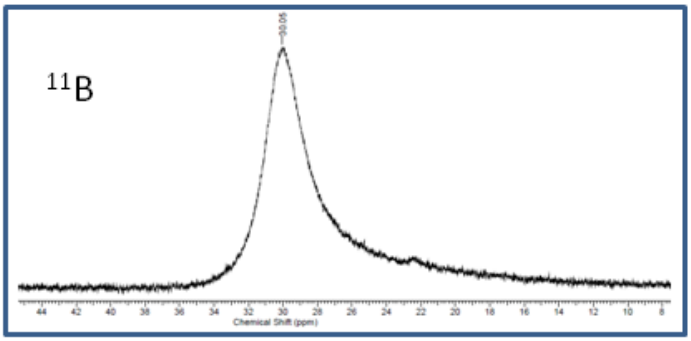
Borylation of *N*-Me indole



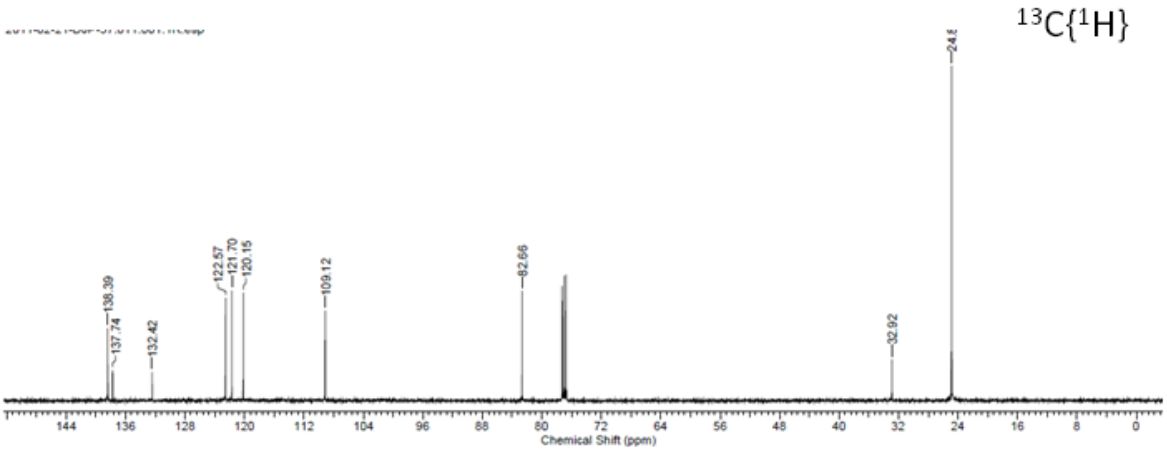
An oven dried 500 mL 3-necked round-bottomed flask cooled under N_2, was charged with B-chlorocatecholborane (18.0 g, 117 mmol, 1 equiv.). This was then dissolved in CH_2Cl_2 (120 mL) and triethylamine (17.1 mL, 123 mmol, 1.05 equiv.) was added dropwise over 20 minutes with care taken not to allow any significant rise in reaction temperature. Over 30 minutes, the resulting solution was transferred via a cannula under a positive pressure of N_2 to an oven dried 1 L 3-necked round-bottomed flask, cooled under N_2, containing a suspension of granular $AlCl_3$ (17.1 g, 129 mmol, 1.1 equiv.) in CH_2Cl_2 (60 mL). The flask was washed with CH_2Cl_2 (20 mL) and to the resulting solution was added *N*-Me indole (13.9 mL, 111 mmol, 0.95 equiv.). The reaction was stirred for 6 hours before being transferred over 45 minutes via a cannula under a positive pressure of N_2 to a solution of pinacol (29.0 g, 246 mmol, 2.1 equiv.) in triethylamine (244 mL, 1.75 mol, 15 equiv.) contained in an oven dried 2 L round-bottomed flask, cooled under N_2, with care taken not to allow any significant rise in reaction temperature. After washing the flask with CH_2Cl_2 (2 × 20 mL) the volatiles were removed *in vacuo*. The resulting beige solid was suspended in pentane (100 mL) and the solids removed by filtration, upon washing with further pentane (5 × 50 mL) the extracts were combined and the volatiles removed *in vacuo* to give the crude product which was purified by chromatography through a short plug of silica gel eluting with 5% EtOAc in petroleum ether 40/60 to give **3m** (25.1 g, 97.6 mmol, 87%) as a pale yellow solid (M.p. 105 - 108 °C).

The NMR data was identical to that previously reported,[1] and representative spectra of the bulk material are shown overpage.

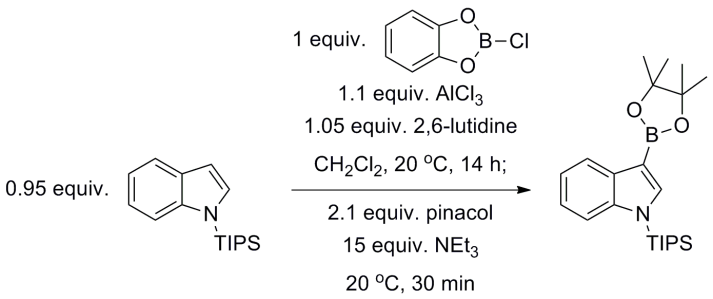

11
10
O
B
O
Hb
Hc
5
4
3
2
Ha
6
Hd
7
8
9
N
1
He


11B
Chemical Shift (ppm)

1H
1
1
1 1 1
3
12
Chemical Shift (ppm)

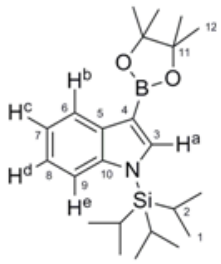

13C{1H}
138.39
137.74
132.42
122.57
121.70
120.15
109.12
82.66
32.92
24.8
Chemical Shift (ppm)

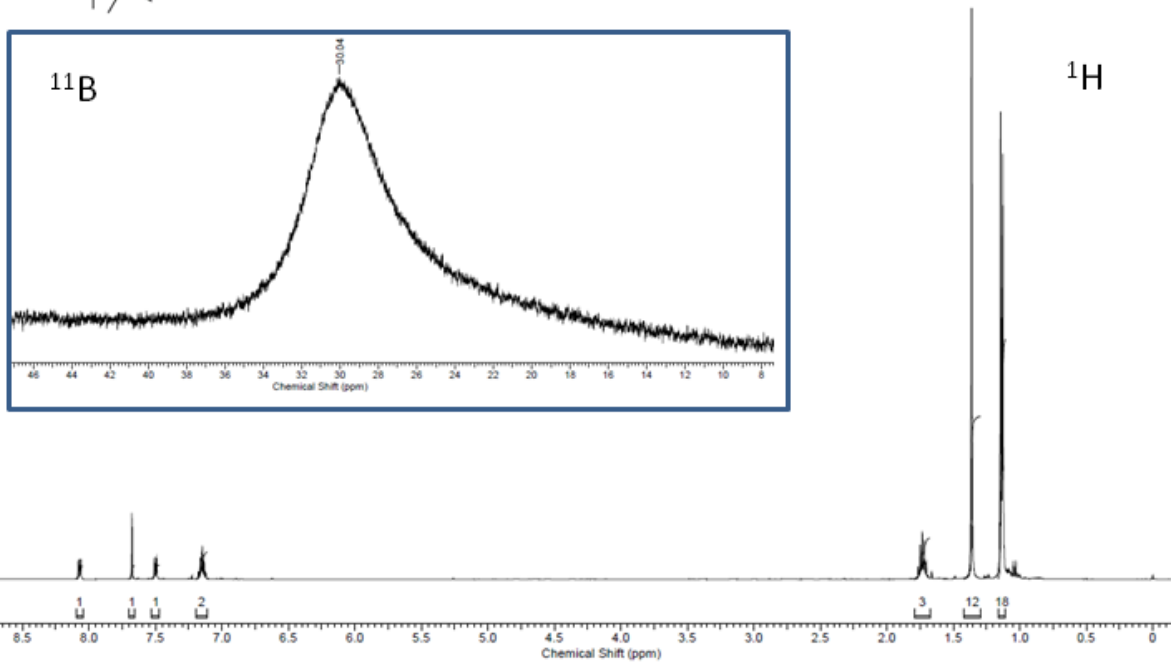
Borylation of *N*-TIPS indole

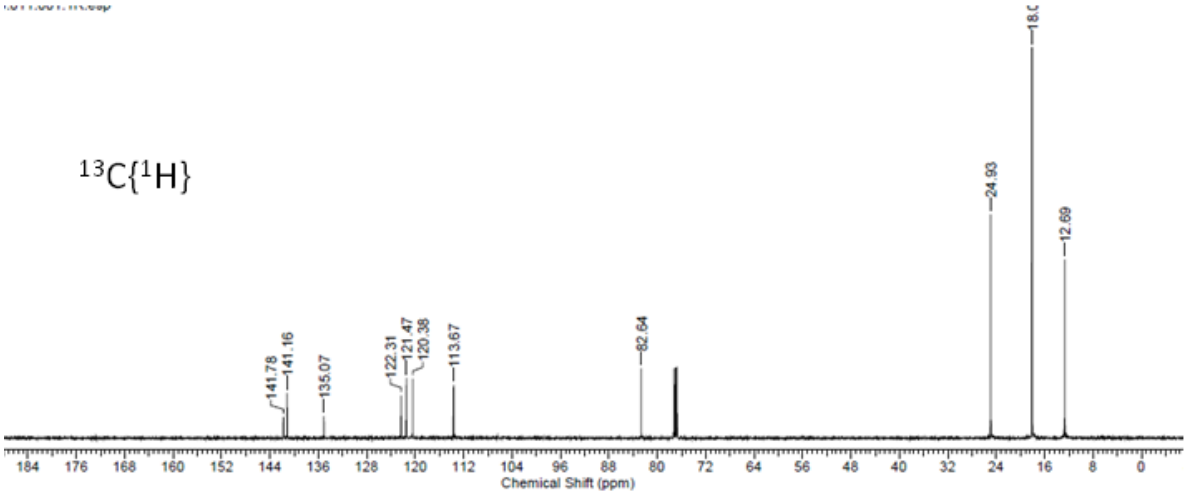


An oven dried 500 mL 3-necked round-bottomed flask cooled under N_2, was charged with B-chlorocatecholborane (17.4g, 113 mmol, 1 equiv.). This was then dissolved in CH_2Cl_2 (120 mL) and 2,6-lutidine (13.7 mL, 118 mmol, 1.05 equiv.) was added dropwise over 20 minutes with care taken not to allow any significant rise in reaction temperature. To the resulting solution was added granular $AlCl_3$ (16.5 g, 124 mmol, 1.1 equiv.) in 5 portions with care taken not to allow any significant rise in reaction temperature. To the resulting solution was added a solution of *N*-TIPS indole (29.3 mL, 107 mmol, 0.95 equiv.) in CH_2Cl_2 (60 mL). The reaction was stirred for 14 hours before being transferred over 45 minutes via a cannula under a positive pressure of N_2 to a solution of pinacol (28 g, 237 mmol, 2.1 equiv.) in triethylamine (236 mL, 1.69 mol, 15 equiv.) contained in an oven dried 2 L round-bottomed flask, cooled under N_2, with care taken not to allow any significant rise in reaction temperature. After washing the flask with CH_2Cl_2 (2 × 20mL) the volatiles were removed *in vacuo*. The resulting beige solid was suspended in pentane (100 mL) and the solids removed by filtration, upon washing with further pentane (5 × 50 mL) the extracts were combined and the volatiles removed *in vacuo* to give the crude product which was purified by chromatography through a short plug of silica gel eluting with petroleum ether 40/60 and then 5% EtOAc in petroleum ether 40/60 to give 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-[triisopropylsilyl]- Indole (34.2 g, 85.6 mmol, 79%) as a colourless solid (M.p. 105 - 107 °C).

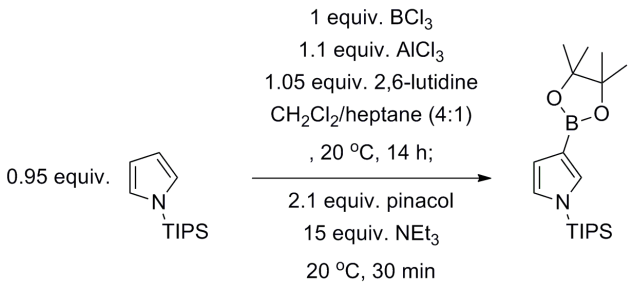
The NMR data was identical to that previously reported,[1] and representative spectra of the bulk material are shown overpage.


Hb
Hc
Ha
Hd
He
O
B
O
N
Si
12
11
10
9
8
7
6
5
4
3
2
1


11B
30.04
Chemical Shift (ppm)
1H
1
1
1
2
3
12
18
Chemical Shift (ppm)

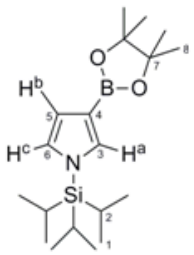

13C{1H}
141.78
141.16
135.07
122.31
121.47
120.38
113.67
82.64
24.93
12.69
Chemical Shift (ppm)

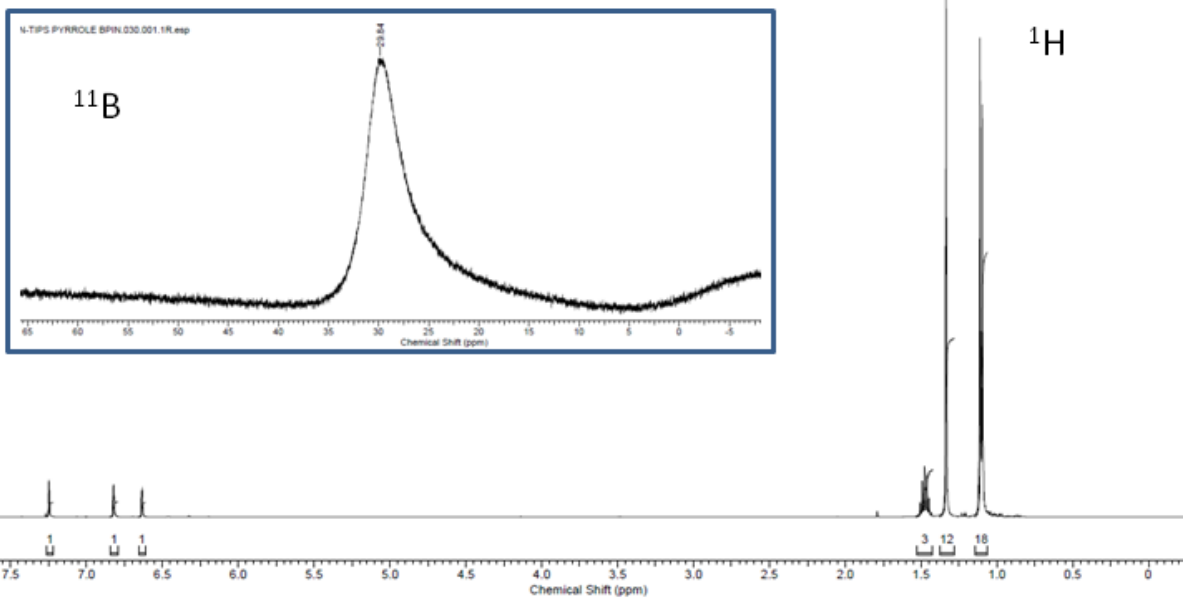
3. Borylation of *N*-TIPS pyrrole

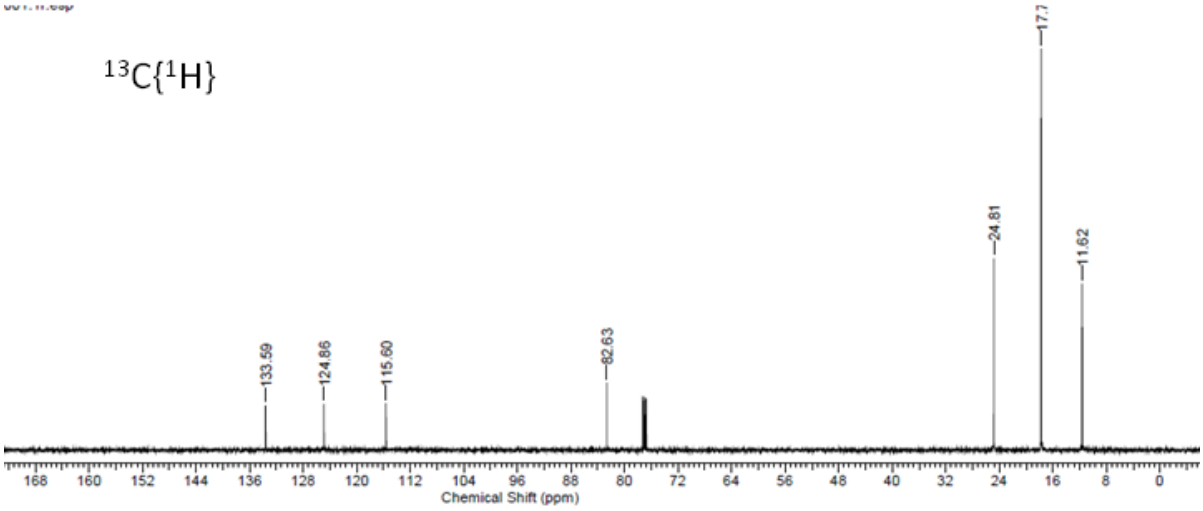


An oven dried 1 L 3-necked round-bottomed flask cooled under N_2, was charged with $AlCl_3$ (10.6 g, 79.3 mmol, 1.1 equiv.). This was then suspended in CH_2Cl_2 (288 mL) and 2,6-lutidine (8.79 mL, 75.7 mmol, 1.05 equiv.) was added. To the resulting suspension was then added a solution of BCl_3 (1.0 M in heptanes, 72.1 mL, 72.1 mmol, 1 equiv.). After 30 minutes a homogeneous yellow solution was obtained to which was added *N*-TIPS pyrrole (15.3 g, 68.5 mmol, 0.95 equiv.). The reaction was stirred for 14 hours before being transferred over 45 minutes via a cannula under a positive pressure of N_2 to a solution of pinacol (17 g, 144 mmol, 2.1 equiv.) in triethylamine (143 mL, 1.03 mol, 15 equiv.) contained in an oven dried 2 L round-bottomed flask, cooled under N_2, with care taken not to allow any significant rise in reaction temperature. After washing the flask with CH_2Cl_2 (2 × 20 mL) the volatiles were removed *in vacuo*. The resulting beige solid was suspended in pentane (100 mL) and the solids removed by filtration, upon washing with further pentane (5 × 50 mL) the extracts were combined and the volatiles removed *in vacuo* to give the crude product which was purified by chromatography on silica gel eluting with petroleum ether 40/60 then 5% EtOAc in petroleum ether 40/60 to give **2m**, 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-[triisopropylsilyl]-pyrrole (21.7 g, 62.1 mmol, 90%) as pale yellow solid (M.p. 67 - 69 °C).

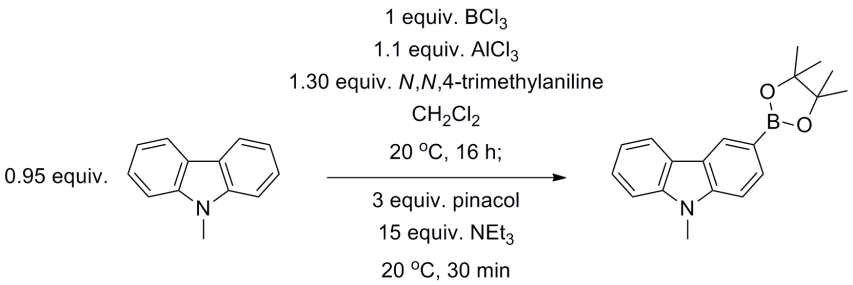
The NMR data was identical to that previously reported,[1] and representative spectra of the bulk material are shown overpage.


O
B–O
H^b
H^c
N
H^a
Si


^{11}B
^{1}H
Chemical Shift (ppm)


^{13}C{^{1}H}
133.59
124.86
115.60
82.63
24.81
17.7
11.62
Chemical Shift (ppm)

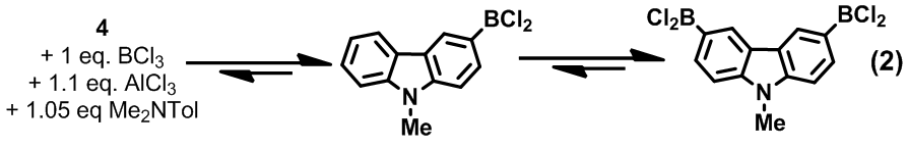
4. Mono-Borylation of *N*-Me carbazole, 4m



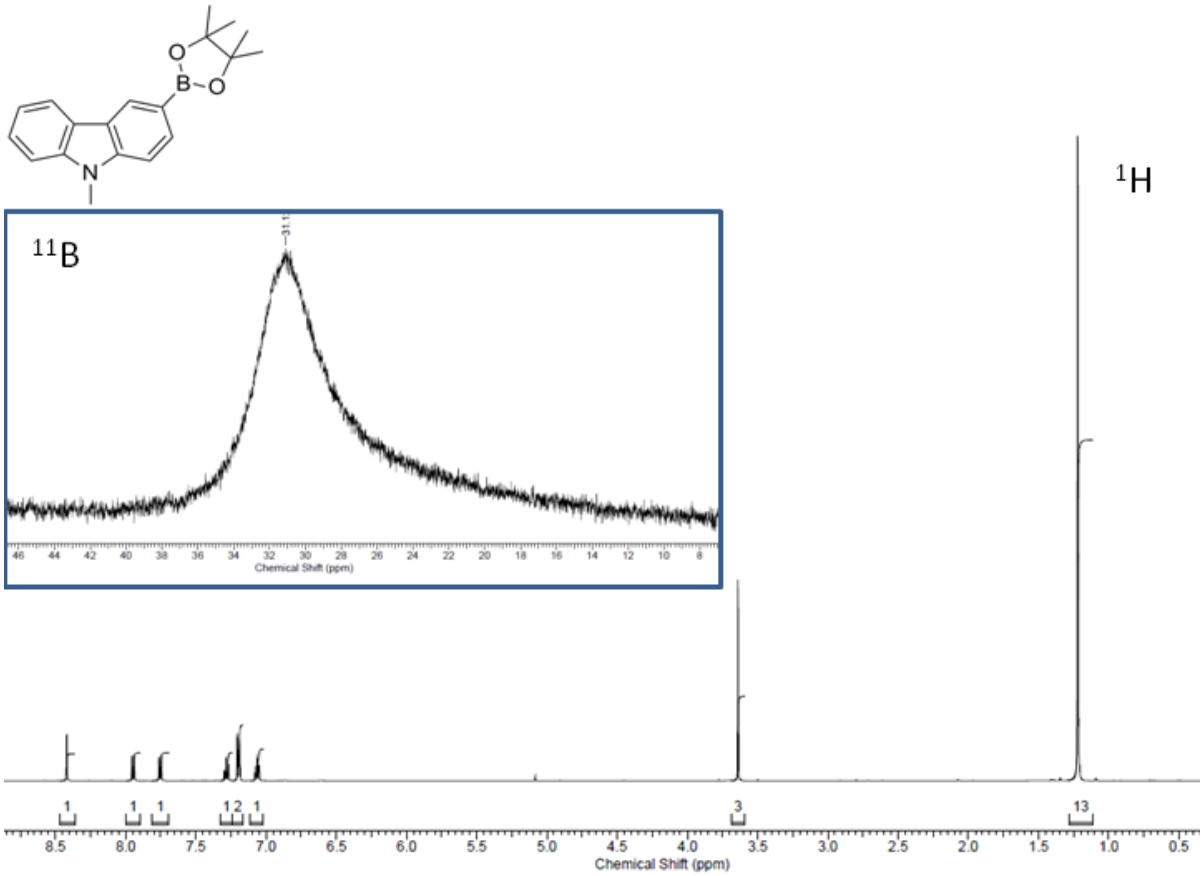
An oven dried 1 L round-bottomed flask cooled under N_2, was charged with $AlCl_3$ (14.7 g, 110 mmol, 1.1 equiv.) and *N*-Me carbazole (17.2 g, 95.0 mmol, 0.95 equiv.). This was then suspended in CH_2Cl_2 (300 mL) and *N*,*N*,4-trimethylaniline (18.8 mL, 130 mmol, 1.3 equiv.) was added. To the resulting solution was then added a solution of BCl_3 (1.0 M in CH_2Cl_2, 100 mL, 100 mmol, 1 equiv.). The reaction was stirred for 16 hours before being transferred over 45 minutes via a cannula under a positive pressure of N_2 to a solution of pinacol (35.5 g, 300 mmol, 3 equiv.) in triethylamine (209 mL, 1.50 mol, 15 equiv.) contained in an oven dried 2 L round-bottomed flask, cooled under N_2, with care taken not to allow any significant rise in reaction temperature. After washing the flask with CH_2Cl_2 (2 × 25 mL) the volatiles were removed *in vacuo* and the resulting beige solid purified by chromatography on silica gel eluting with a gradient of 0 - 20% EtOAc in petroleum ether 40/60 to give **4m** (22.3 g, 72.6 mmol, 76%) as a pale yellow solid (M.p. 147 - 149 °C).

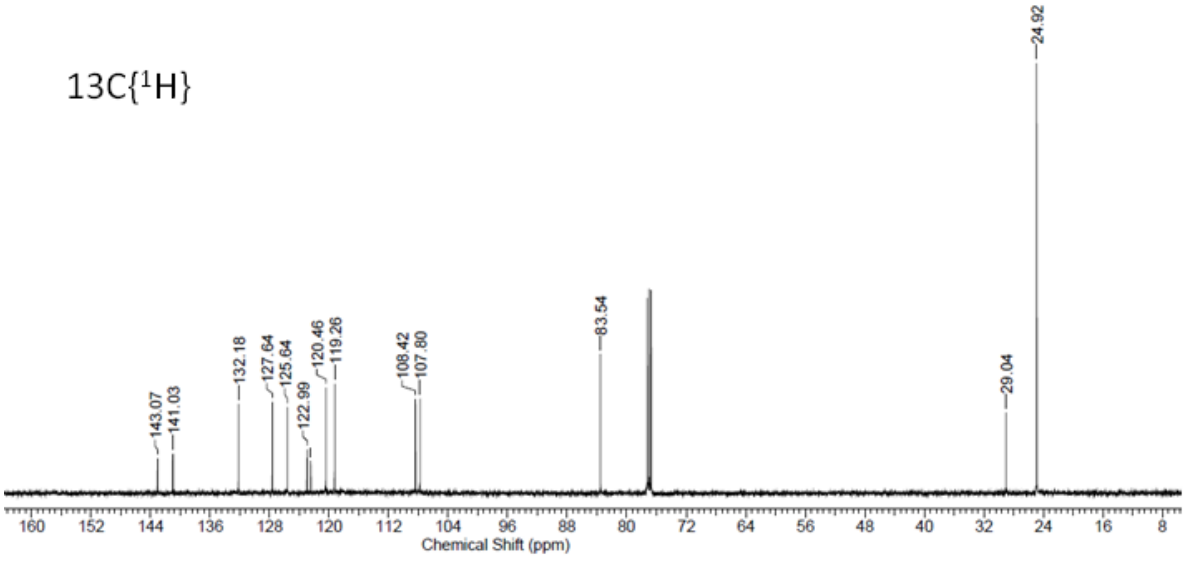
The NMR data was identical to that previously reported,[1] and representative spectra of the bulk material are shown overpage.

A slight excess of Me_2Ntol is essential to prevent Brønsted acid initiated B-C bond cleavage in the initial 3-(BCl_2)-*N*-Me-carbazole product. Base deficient conditions led to the formation of 3,6-diborylated carbazole **4d**, as a minor product on work up along with **4m** as the major product (e.g., 11 % of **4d** was isolated after 1 hour borylation duration using 1 : 1.1 : 1.05 BCl_3 : $AlCl_3$: Me_2Ntol). The increase in 3,6-(BCl_2)$_2$-*N*-Me-carbazole with time under base deficient conditions is due to the lower arene nucleophilicity of di-borylated species resulting in slower protodeboronation compared



to mono-borylated compounds e.g., 3-(BCl_2)-*N*-Me-carbazole (eq. 2).


11B
31.1
Chemical Shift (ppm)
1H
1 1 1 1 2 1 3 13
Chemical Shift (ppm)


13C{1H}
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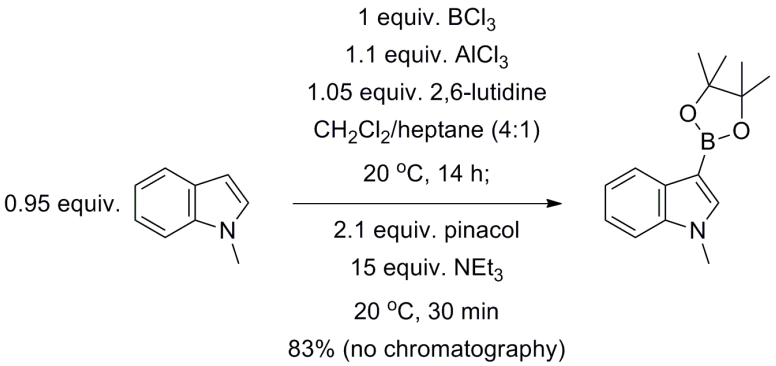
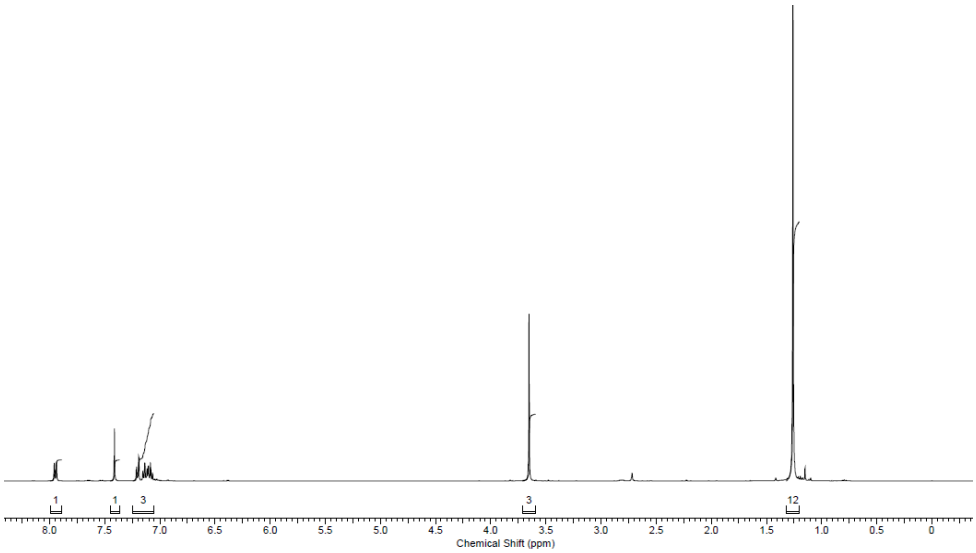
141.03
132.18
127.64
125.64
122.99
120.46
119.26
108.42
107.80
83.54
29.04
24.92
Chemical Shift (ppm)

Screening of substrate scope using BCl_3 derived boron electrophiles.

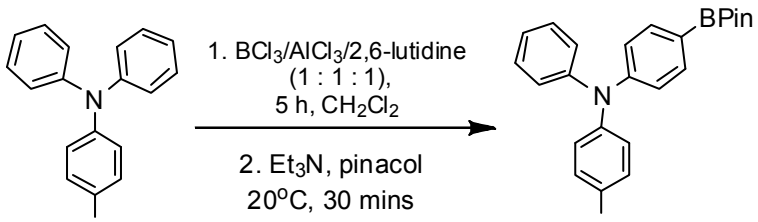
1-methyl-3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-indole, 3m



An oven dried 50 mL 3-necked round-bottomed flask cooled under N_2, was charged with $AlCl_3$ (440 mg, 3.3 mmol, 1.1 equiv.). This was then suspended in CH_2Cl_2 (10 mL) and 2,6-lutidine (0.366 mL, 3.15 mmol, 1.05 equiv.) was added. To the resulting suspension was then added a solution of BCl_3 (1.0 M in heptanes, 3 mL, 3 mmol, 1 equiv.). After 30 minutes a homogeneous yellow solution was obtained to which was added *N*-Me Indole (374 mg, 2.85 mmol, 0.95 equiv.). The reaction was stirred for 14 hours before being transferred by cannula under a positive pressure of N_2 to a solution of pinacol (745 mg, 6.3 mmol, 2.1 equiv.) in triethylamine (6.3 mL, 45 mmol, 15 equiv.) contained in an oven dried 100 mL round-bottomed flask, cooled under N_2, with care taken not to allow any significant rise in reaction temperature. After washing the flask with CH_2Cl_2 (2 × 20 mL) the volatiles were removed *in vacuo*. The resulting beige solid was suspended in pentane (30 mL) and the solids removed by filtration, upon washing with further pentane (5 × 5 mL) the extracts were combined and the volatiles removed *in vacuo* to give the product, **3m**, (607 mg, 2.36 mmol, 83%) as pale yellow solid. Below is a representative ^1H NMR spectrum of the product isolated from this reaction.

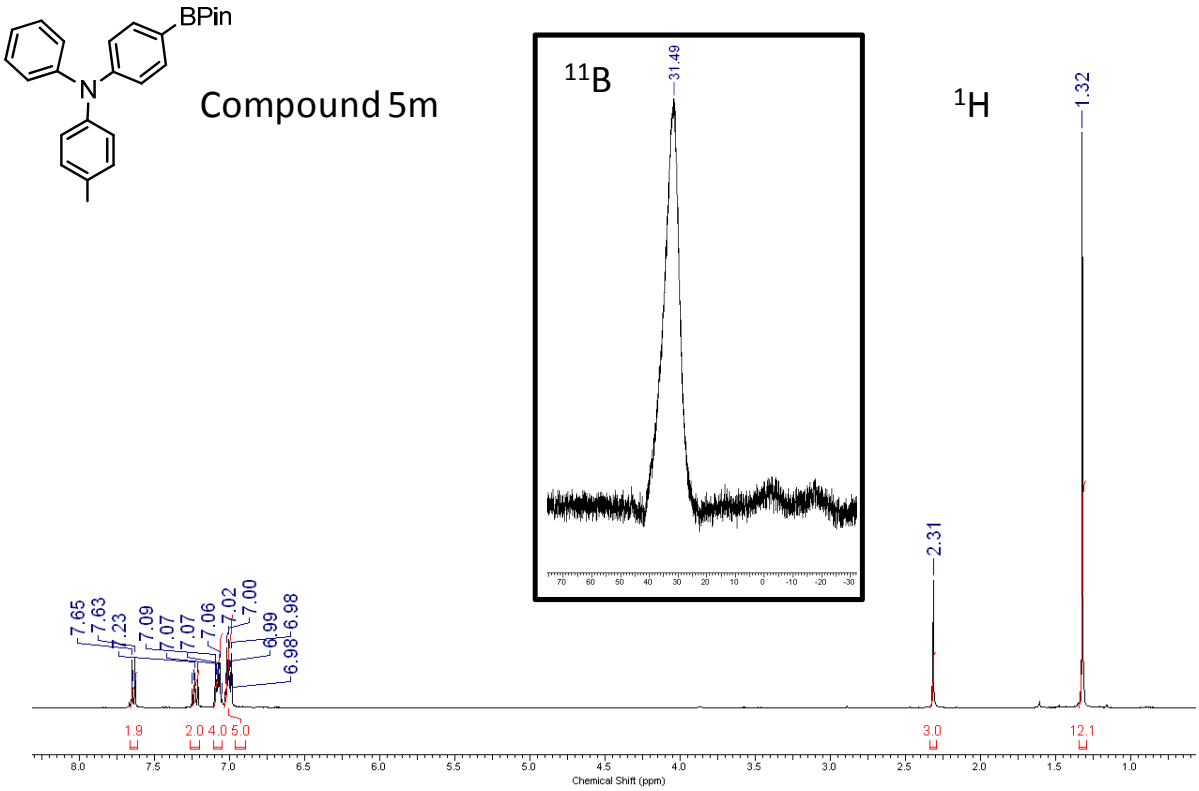


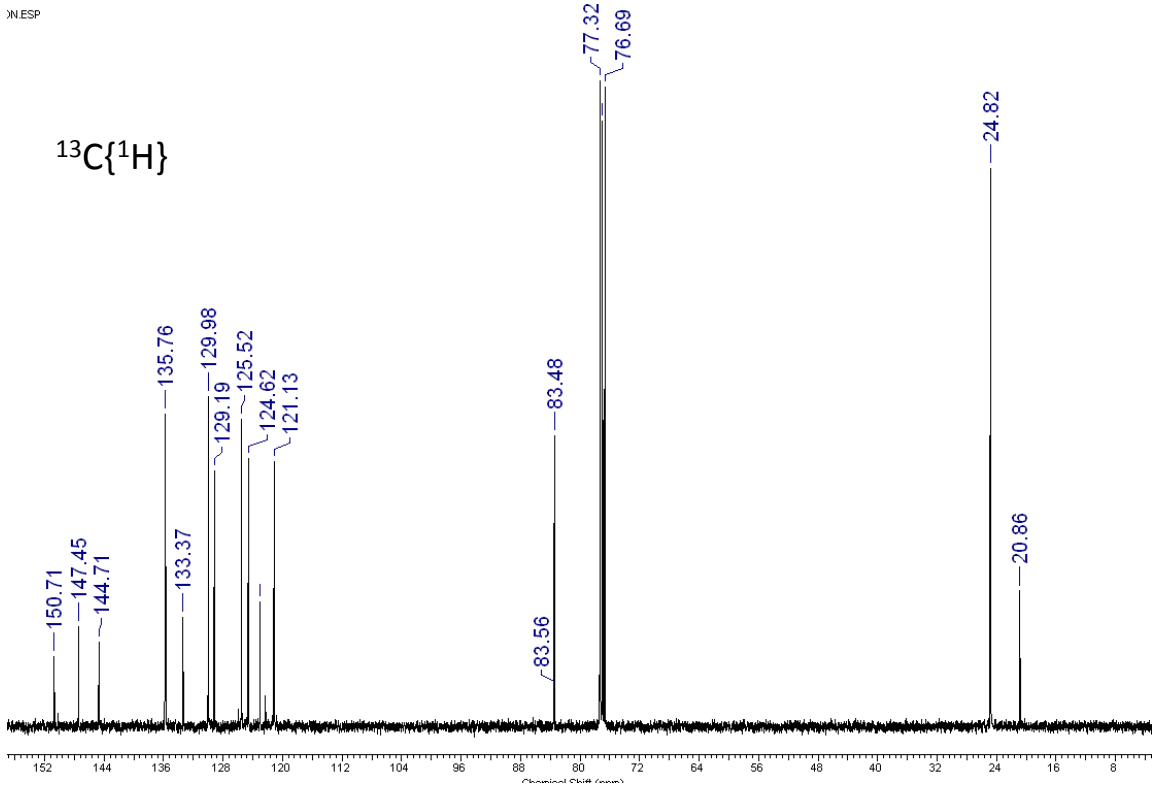
N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-Ph)-N-Ph-4-methyl-aniline, 5m



BCl_3 : $AlCl_3$: 2,6-lutidine : Ph_2NTol: An oven dried Young's NMR tube, was charged with 2,6-lutidine (23 µl, 21 mg, 0.20 mmol, 1 equiv.) in dry CH_2Cl_2 (0.7 ml). This was then treated with $AlCl_3$ (27 mg, 0.20 mmol, 1 equiv.), BCl_3 (0.22 ml, 0.20 mmol, 0.9 M soln, CH_2Cl_2) and *N,N'*-diphenyl-p-toluidine (52 mg, 0.20 mmol, 1 equiv.) to give a light green solution. The reaction was left to stir for 5 hrs at room temperature. The solution was treated with triethylamine (0.42 ml, 3.0 mmol, 15 equiv.) and pinacol (50 mg, 0.42 mmol, 2.1 equiv.) and stirred to give an orange suspension, which was left to stir for 30 mins. The mixture is poured into a round-bottomed flask, and the NMR tube washed with CH_2Cl_2. The washings are combined with the suspension in the round-bottomed flask. CH_2Cl_2 and triethylamine are removed under vacuum. Excess 2,6-lutidine/pinacol and *N,N'*-diphenyl-p-toluidine removed by flash column chromatography with pet. ether/ether, slowly increasing solvent polarity. Fractions containing product are combined and the solvents removed under vacuum to give a colourless solid (63 mg, 82 %)

^{1}H NMR ($CDCl_3$): δ 1.32 (s, 12H, 4 × Me, pinacol), 2.31 (s, 3H, -C_6H_4Me), 7.00 (m, 5H, ArH), 7.07 (m, 4H, ArH), 7.23 (m, 2H, ArH), 7.64 (d, ^3J= 8.0 Hz, 2H, ArH). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 20.86 (1 × Me), 24.82 (4 × Me, pinacol), 83.48, 121.13, 123.03, 124.62, 125.52, 129.19, 129.98, 133.37, 135.76, 144.71, 147.45, 150.71. ^{11}B NMR ($CDCl_3$): δ 31.49 (s, broad).


BPin
N
Compound 5m
11B
31.49
1H
1.32
2.31
7.65
7.63
7.23
7.09
7.07
7.07
7.06
7.02
7.00
6.99
6.98
6.98
1.9
2.0
4.0
5.0
3.0
12.1
Chemical Shift (ppm)


13C{1H}
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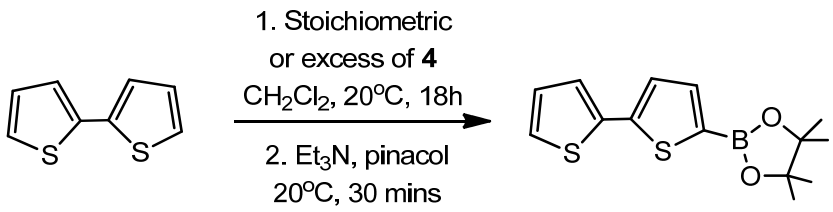
76.69
24.82
135.76
129.98
129.19
125.52
124.62
121.13
83.48
150.71
147.45
144.71
133.37
83.56
20.86

5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2'-dithiophene, 6m



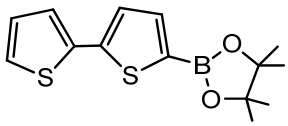
An oven dried Young's NMR tube, was charged with 2,6-lutidine (42 µl, 0.36 mmol, 2.10 equiv.) in dry CH_2Cl_2 (0.4 ml). This was then treated with $AlCl_3$ (49 mg, 0.37 mmol, 2.20 equiv.), BCl_3 (0.34 ml, 0.34 mmol, 1.0 M solution in CH_2Cl_2, 2.00 equiv.) and 2,2'-bithiophene (27 mg, 0.16 mmol, 0.95 equiv.) to give a light green solution. The reaction was left to rotate for 18 hrs, to give a dark green solution. The solution was treated with triethylamine (0.72 ml, 5.1 mmol, 30 equiv.) and pinacol (80 mg, 0.68 mmol, 4.2 equiv.) and stirred to give an orange suspension, which was left to stir for 30 mins. The suspension was transferred to a Schlenk and the NMR tube washed with dry CH_2Cl_2 (3 × 1 ml). The CH_2Cl_2 was removed under vacuum and dried for 1 hr, and replaced with dry pentane (10 ml) to give an orange suspension. The suspension was filtered, via cannula, through a plug of celite to give a colourless solution. The celite was washed with pentane (5 × 2 ml). The pentane was removed under vacuum to give a pale yellow colourless oil (40 mg, 86%).

The NMR data was identical to that previously reported,[2] and a representative ^{1}H and ^{11}B NMR spectra are shown overpage.

Leaving this reaction for longer resulted in no growth of the 5,5'-diborylated product.

For monoborylation the number of equivalents of BCl_3/$AlCl_3$/2,6-lutidine can be reduced down to 1.2 : 1.3 : 1.4 BCl_3 : 2,6-lutidine : $AlCl_3$, with concomitant reduction in the quantity of pinacol to 3 equivalents of pinacol.

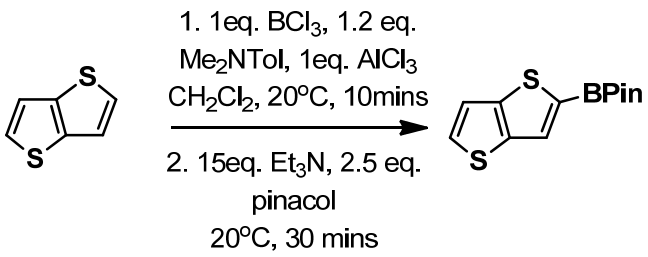
Compound 6m



1.35
13.6
7.01
7.02
7.03
7.23
7.24
7.26
7.52
7.53
1.0
3.1
1.1
Chemical Shift (ppm)
-SS33 PROTON.ESP

11B
29.4
Chemical Shift (ppm)

5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-thieno-[3,2-b]-thiophen-2-yl, 7m



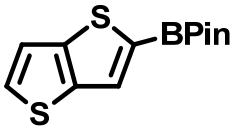
BCl_3 (1M in CH_2Cl_2) (0.2mL, 1eq, 0.2 mmol), *N,N*-dimethyl *p*-toluidine (31µL, 1.2eq, 0.24mmol) and dry CH_2Cl_2 (0.2 mL) were added by syringe to a J. Youngs NMR tube. $AlCl_3$ (25mg, 1eq. 0.2mmol) and thieno[3,2-b]thiophene (26mg, 1eq. 0.2mmol) were added consecutively as solids. After 10 minutes, the NMR tube was charged with triethylamine (0.4mL, 15eq 3mmol) followed by addition of pinacol (55mg, 2.5eq, 0.5mmol). The suspension was extracted into a Schlenk, the NMR tube was washed with CH_2Cl_2 (2mL) and the resulting mixture was evaporated under vacuum. To the resulting solid, hexane (3mL) was added and the mixture was sonicated for 1 minute. The solids were removed by filtration, upon washing with further hexane (3mL), the extracts were combined and the volatiles removed in vacuum to give the crude product which was purified by flash chromatography through a short plug of neutral alumina using hexane as solvent to give a colourless crystalline solid. Isolated Yield: 81%

The NMR data was identical to that previously reported,[3] and representative NMR spectra are shown overpage.

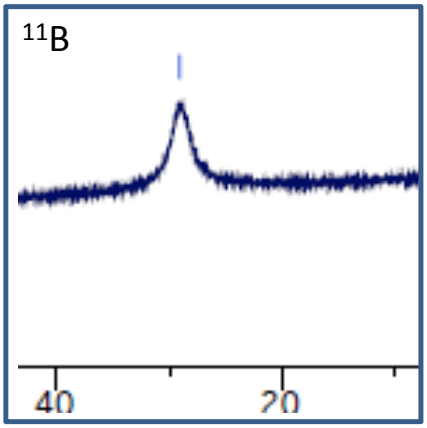
^{1}H NMR ($CDCl_3$): δ 7.76 (s, 1H), 7.48 (d, *J*= 5.2Hz, 1H), 7.28 (d, *J*= 5.2 Hz, 1H), 1.36 (s, 12H).

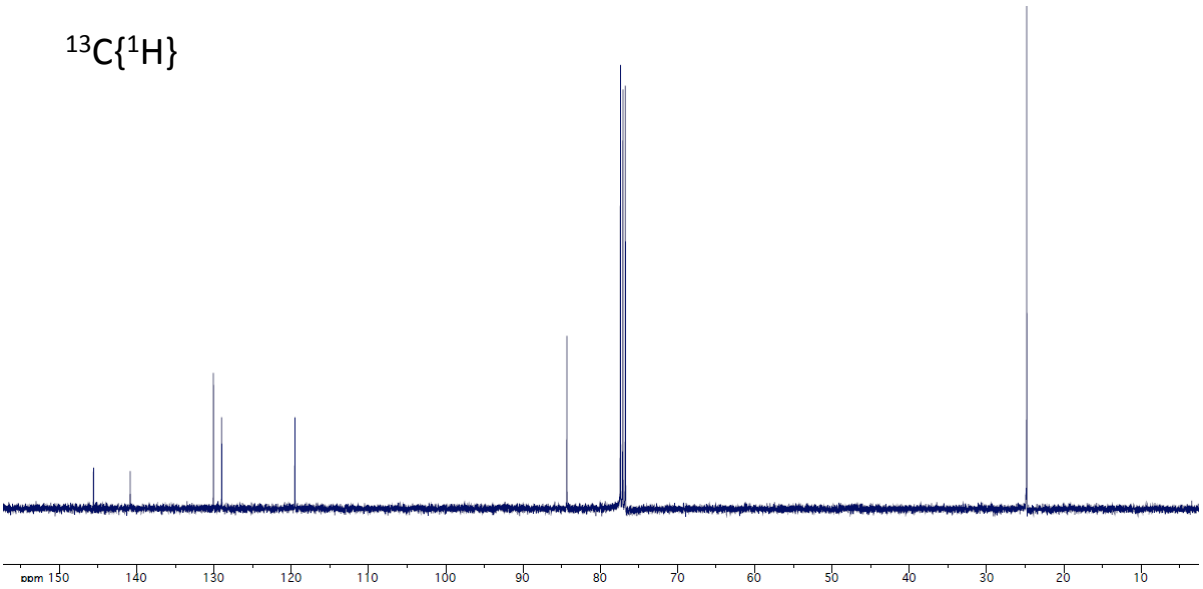
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 145.6, 140.1, 130.0, 129.0, 128.9, 119.5, 84.3, 24.9, 24.8.

^{11}B NMR ($CDCl_3$): δ 29.1



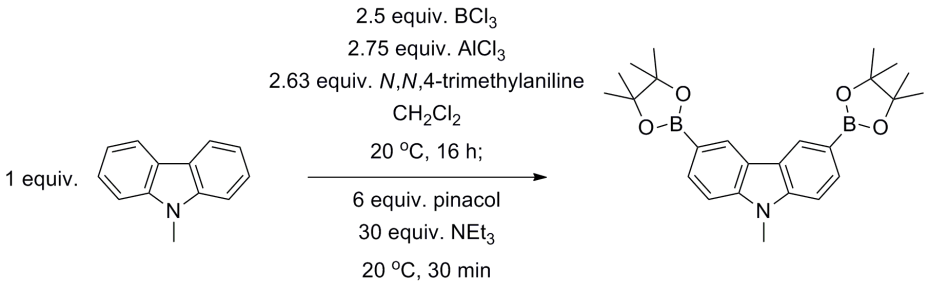
Compound 7m





Diborylation of *N*-Me carbazole:

3,6-Di(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9-methylcarbazole, 4d



An oven dried 25 mL round-bottomed flask cooled under N_2, was charged with $AlCl_3$ (117 mg, 0.880 mmol, 2.75 equiv.) and *N*-Me carbazole (58 mg, 0.320 mmol, 1 equiv.). This was then suspended in CH_2Cl_2 (3 mL) and *N*,*N*,4-trimethylaniline (121 µL, 0.840 mmol, 2.625 equiv.) was added. To the resulting solution was then added a solution of BCl_3 (1.0 M in CH_2Cl_2, 0.8 mL, 0.800 mmol, 2.5 equiv.). The reaction was stirred for 16 hours before being transferred over 15 minutes via a cannula under a positive pressure of N_2 to a solution of pinacol (227 mg, 1.92 mmol, 6 equiv.) in triethylamine (1.34 mL, 9.60 mmol, 30 equiv.) contained in an oven dried 50 mL round-bottomed flask, cooled under N_2, with care taken not to allow any significant rise in reaction temperature. After washing the flask with CH_2Cl_2 (2 × 25 mL) the volatiles were removed *in vacuo* and the resulting beige solid purified by chromatography on silica gel eluting with a gradient of 10 - 20% EtOAc in hexane to give **4d** (84 mg, 0.194 mmol, 60%) as a pale yellow solid (M.p. 257 - 259 °C).

Whilst this compound has been reported before the spectroscopic data was not, therefore it is included in full below.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.7 (2 H, s), 7.9 (2 H, dd, *J* = 8.3, 1.0 Hz), 7.4 (2 H, d, *J* = 8.3 Hz), 3.9 (3 H, s), 1.4 (24 H, s) ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 132.1, 127.9, 122.7, 107.8, 83.5, 29.1, 24.9 ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.1

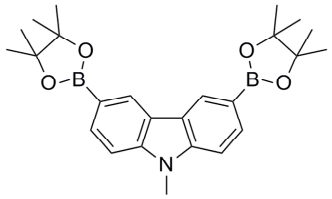
ν_{max} (liquid film)/cm^{-1} 2979w (C-H), 2930w (C-H), 1625w, 1597w, 1468w, 1351s (B-O), 1318m, 1258w, 1145m, 1083w

MS (ES$^+$) *m/z* (%) 434 (100 [M + H]$^+$), 352 (10 [M + H - C_6H_{11}]$^+$), 308 (5, [M + H – BPin], 264 (50); Calcd for $C_{25}H_{34}B_2NO_4F_3$ [M + H]$^+$: 434.2669, found: *m/z* 434.2666.

The NMR data was similar to that previously reported for the 9-butyl analogue, 3,6-Di(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9-butylcarbazole,[4] and representative NMR spectra of **4d** are

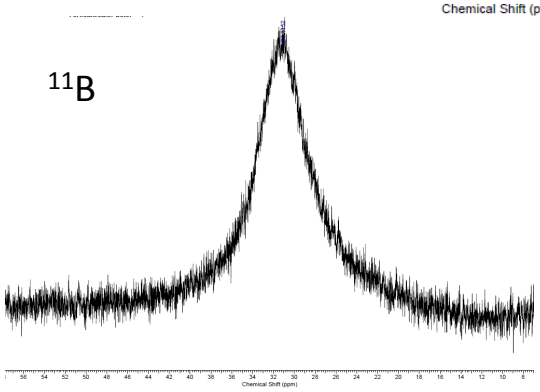
shown overpage.

Compound 4d



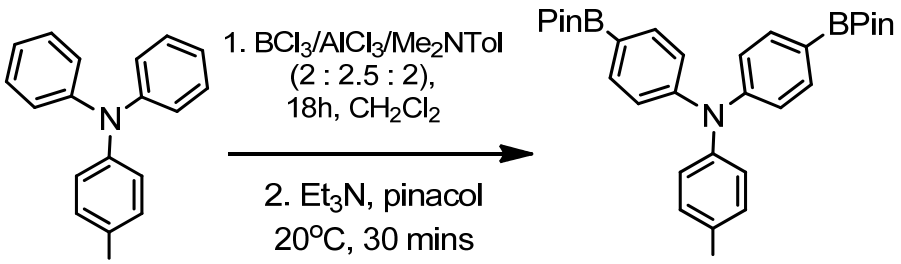
^{1}H

^{11}B



$^{13}C\{^{1}H\}$

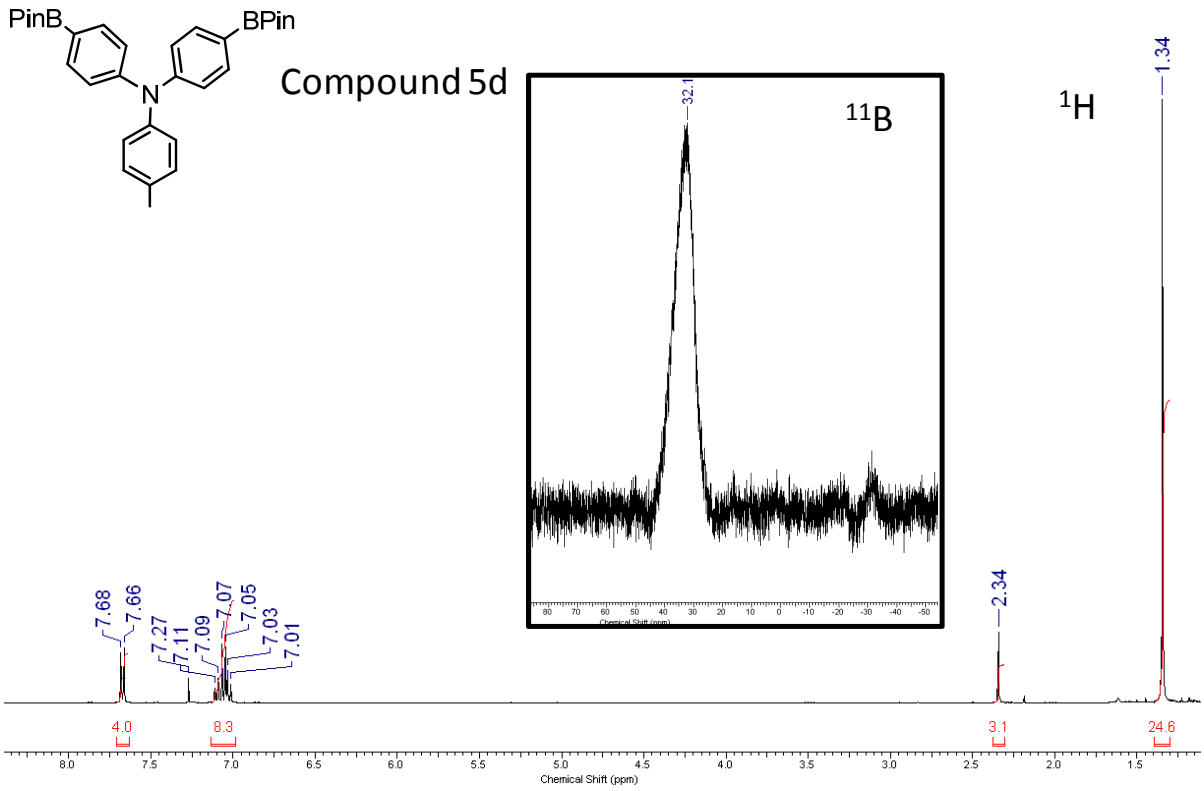
_N,N_-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-Ph)$_2$-4-methyl-aniline, 5d.

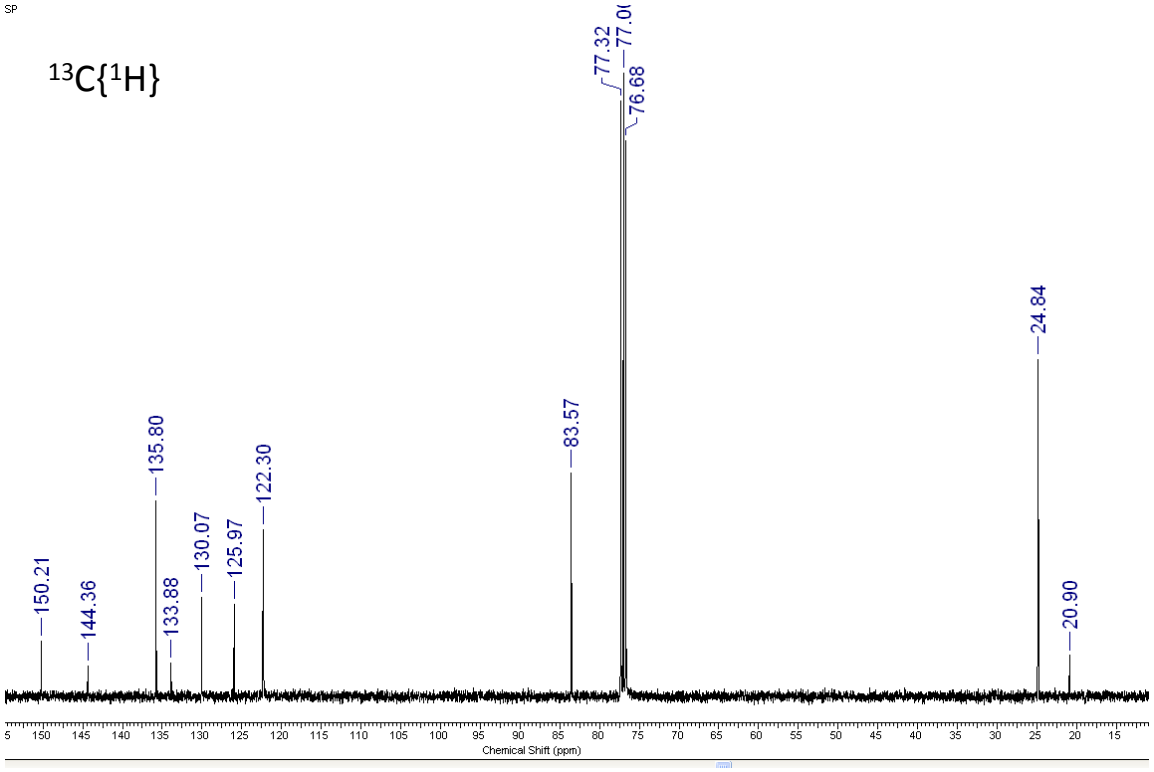


A Schlenk, was charged with $(Me_2NTol)BCl_3$ adduct (151 mg, 0.60 mmol, 2 equiv.) in dry CH_2Cl_2 (3 ml). This was then treated with $AlCl_3$ (100 mg, 0.75 mmol, 2.5 equiv.), Me_2NTol (30 µl, 28 mg, 0.21 mmol, 0.7 equiv.) and *N,N'*-diphenyl-p-toluidine (78 mg, 0.3 mmol, 1 equiv.) to give a light green solution. The reaction was left to stir for 18 hrs at room temperature. The solution was treated with triethylamine (1.26 ml, 9 mmol, 30 equiv.) and pinacol (166 mg, 1.42 mmol, 4.7 equiv.) and stirred to give an orange suspension, which was left to stir for 30 mins. The mixture is poured into a round-bottomed flask, and the NMR tube washed with CH_2Cl_2. The washings are combined with the suspension in the round-bottomed flask. CH_2Cl_2 and triethylamine are removed under vacuum. Excess Me_2NTol/pinacol and *N,N'*-diphenyl-p-toluidine removed by flash column chromatography with pet. ether/ether, slowly increasing solvent polarity. Fractions containing product are combined and the solvents removed under vacuum to give a colourless solid (124mg, 81%)

^{1}H NMR ($CDCl_3$): δ 1.34 (s, 24H, 4 × Me, pinacol), 2.34 (s, 3H, -C_6H_4Me), 7.06 (m, 8H, ArH), 7.67 (d, ^3J= 8.0 Hz, 4H, ArH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 20.90 (1 × Me), 24.84 (4 × Me, pinacol), 83.57, 122.30, 125.97, 130.07, 133.88, 135.80, 144.36, 150.21. ^{11}B NMR ($CDCl_3$): δ 32.19 (s, broad).

^{1}H NMR and $^{13}C\{^1H\}$ resonances are comparable to that previously reported.[5]


PinB
BPin
N
Compound 5d
11B
32.1
1H
1.34
7.68
7.66
7.27
7.11
7.09
7.07
7.05
7.03
7.01
2.34
4.0
8.3
3.1
24.6
Chemical Shift (ppm)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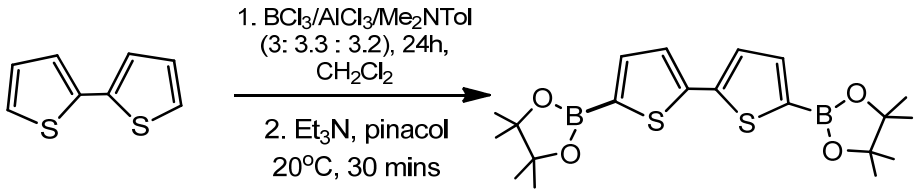
77.0
76.68
24.84
135.80
83.57
122.30
130.07
125.97
150.21
144.36
133.88
20.90
Chemical Shift (ppm)

5,5'-Di-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2'-dithiophene, 6d



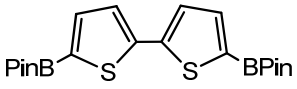
An oven dried J. Young's NMR tube, was charged with *N*,*N*-Dimethyl-*p*-toluidine (58 µl, 0.40 mmol, 3.15 equiv.) in dry CH_2Cl_2 (0.4 ml). This was then treated with $AlCl_3$ (56 mg, 0.42 mmol, 3.30 equiv.), BCl_3 (0.38 ml, 0.38 mmol, 1.0 M solution in CH_2Cl_2, 3.00 equiv.) and 2,2'-bithiophene (21 mg, 0.13 mmol, 1.00 equiv.) to give an orange/brown solution. The reaction was left to rotate for 24 hrs, to give a dark green solution. The solution was treated with triethylamine (0.54 ml, 3.84 mmol, 30 equiv.) and pinacol (110 mg, 0.93 mmol, 7.3 equiv.) and rotated to give an orange suspension, which was left to stir for 30 mins. The suspension was transferred to a schlenk and the NMR tube washed with dry CH_2Cl_2 (3 × 1 ml), and the washings transferred to the schlenk. The CH_2Cl_2 was removed under vacuum and dried for 1 hr, and replaced with dry pentane (10 ml) to give an orange suspension. The suspension was filtered, via cannula, and the solid was washed with pentane (2 × 10 ml). The combined pentane extracts were removed under vacuum to give a very pale yellow solid, which was washed with methanol (3 × 2 ml) and dried for three hours to give a yellow solid (44 mg, 83%). Yield quoted is based upon dithiophene.

^{1}H NMR and $^{13}C\{^{1}H\}$ resonances are comparable to that previously reported.[6]

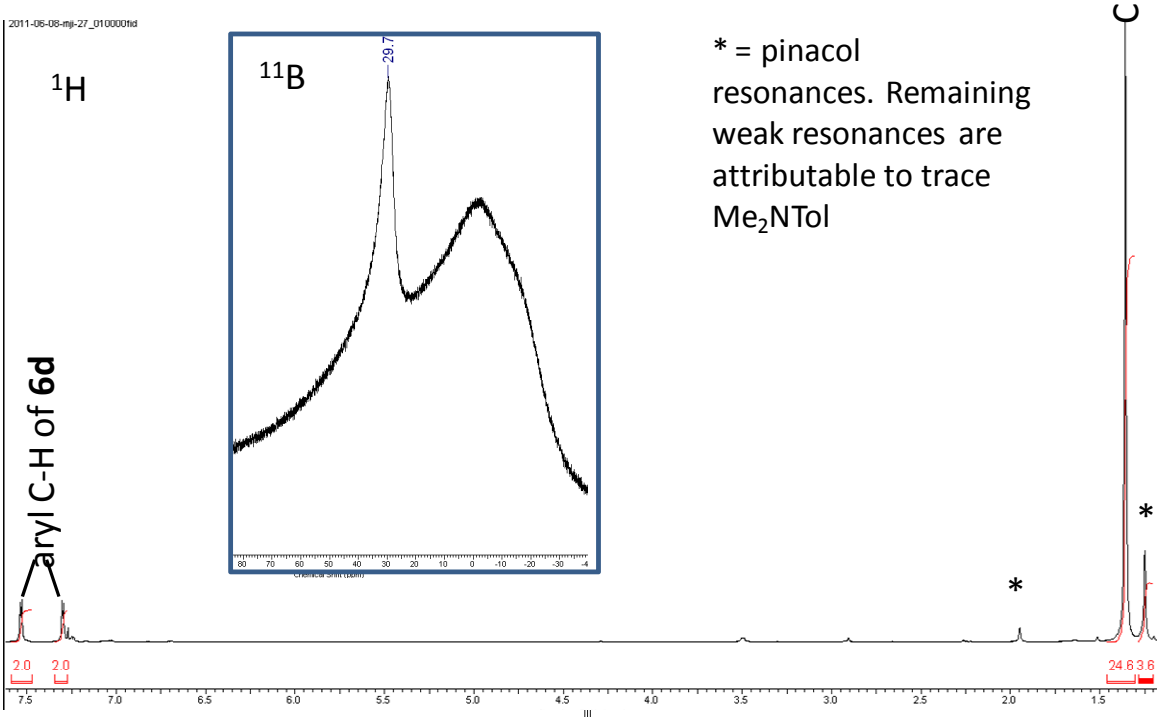
The NMR spectra overpage are for **6d** purified simply by removal of all solvents from the crude reaction mixture post esterification, extraction with pentane and drying for 18h at $1x10^{-2}$ torr, to remove residual Me_2NTol. If necessary to obtain higher purity and remove all pinacol then this is facilely achieved either:

a) filtration through a plug of silica (pretreated with 10% Et_3N in CH_2Cl_2) or alumina.

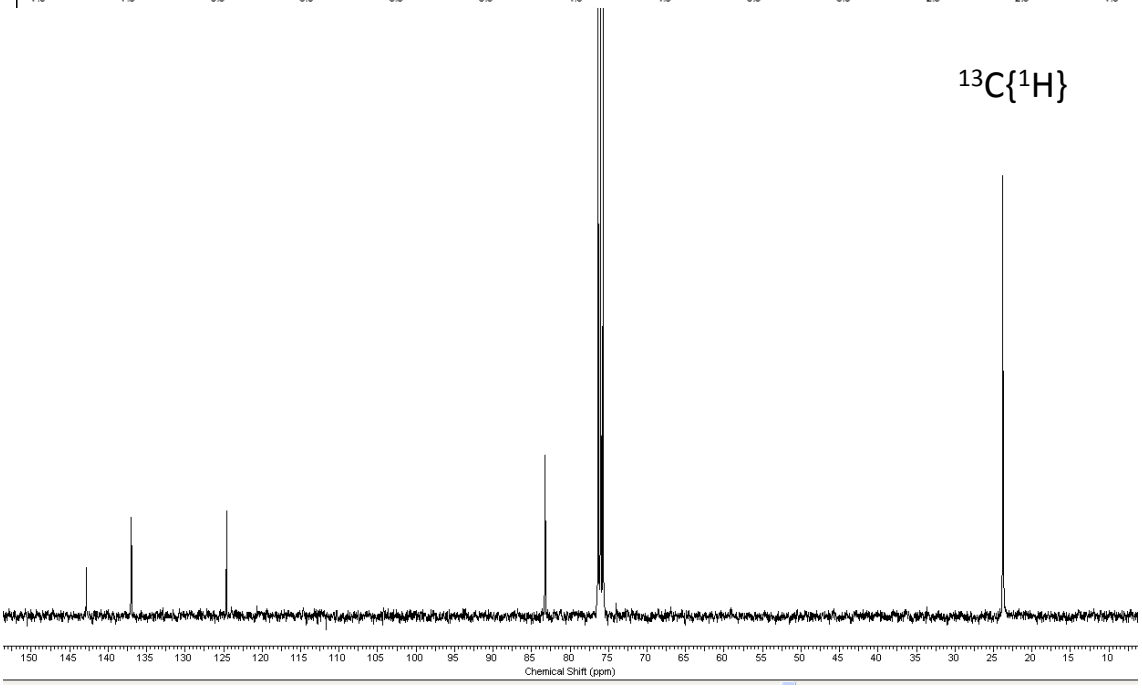
b) washing with a small quantity of methanol (as in the above prep.) in which 6d is poorly soluble. This is also useful for removal of any traces of monoborylated product **6m**, which is significantly more soluble in methanol than **6d**.



Compound 6d



* = pinacol resonances. Remaining weak resonances are attributable to trace Me_2NTol



Borylation of *m*-Xylene:

An oven dried Young's NMR tube, was charged with BCl_3-DMT adduct (63 mg, 0.25 mmol, 1.1 equiv.) in dry *o*-dichlorobenzene (0.8 ml). This was then treated with $AlCl_3$ (33 mg, 0.25 mmol, 1.1 equiv.) and *m*-xylene (28 µl, 24 mg, 0.23 mmol, 1.0 equiv). The solution was heated to 140°C for 3 days. ^{11}B NMR suggested 56% conversion after 18hrs at 140°C, however only 72 % conversion after 2 days of heating, and no/little change after the third day of heating.

Work Up:

The solution was treated with triethylamine (0.48 ml, 349mg, 3.45 mmol, 15 equiv) and pinacol (60 mg, 0.51 mmol, 2.2 equiv.) and stirred to give an orange suspension, which was left to stir for 30 mins. The suspension was transferred to a round bottomed flask and the NMR tube washed with dry CH_2Cl_2 (3 × 2 ml) and combined in the flask. The CH_2Cl_2 was removed under vacuum at room temperature, and the dichlorobenzene removed under vacuum at 40°C for 15 mins to give a sticky solid. The solid was washed with hexane (25 ml) to give an orange suspension. The suspension was filtered to give a colourless solution, hexane was removed under vacuum and the product dried overnight to give the crude pinacol-borylated xylene (26mg, 49% yield). The crude ^{1}H NMR showed the presence of both 1,3,5-borylated-*m*-xylene and the 1,2,4-borylated-*m*-xylene. See below for NMR.

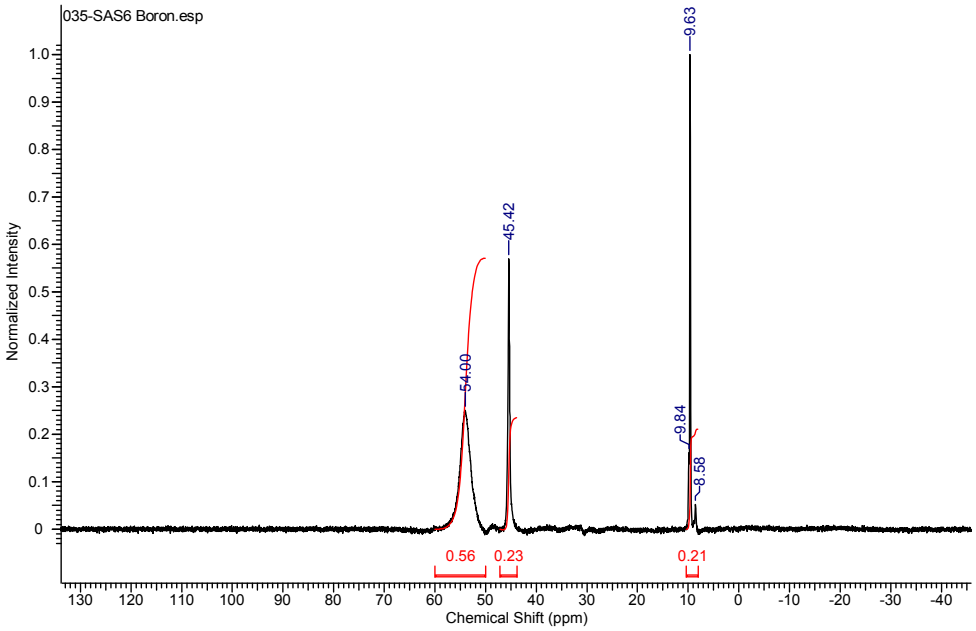
Independently synthesised standards for each isomer were synthesised from the boronic acid by addition of one equivalent of pinacol in pentane in the presence of $MgSO_4$. Stirring overnight was followed by filtration and removal of solvent in-vacuo to afford the desired pinacolato boronate ester in high yield.

Control Reaction - Borylation of *m*-Xylene:

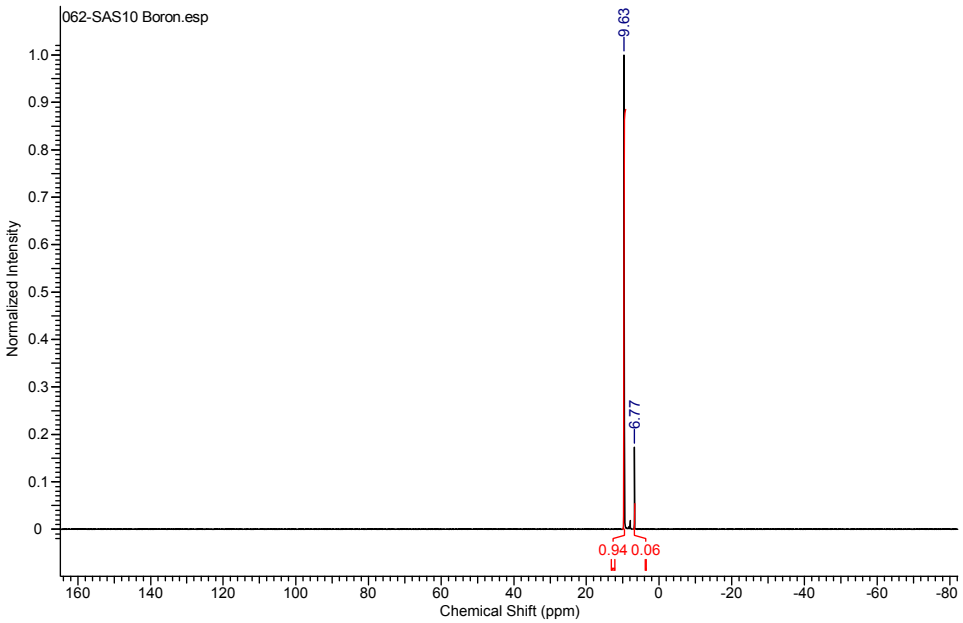
An oven dried Young's NMR tube, was charged with BCl_3-DMT adduct (63 mg, 0.25 mmol, 1.1 equiv.) in dry *o*-dichlorobenzene (0.8 ml). This was then treated with *m*-xylene (28 µl, 24 mg, 0.23 mmol, 1.0 equiv). The solution was heated to 140°C for 20 hrs. ^{11}B NMR showed no reaction after 20 hrs, however if $AlCl_3$ is present after 18 hrs at 140°C there is 56% conversion. See below for comparative NMR.

NMR Spectra:

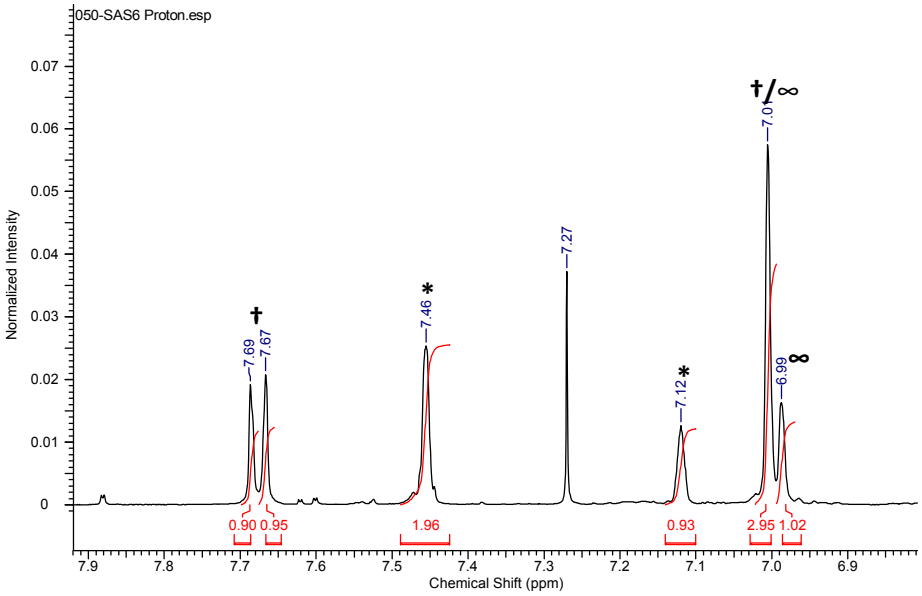
^{11}B NMR Spectrum of in-situ borylation of *m*-xylene after 18 hrs at 140°C with BCl_3 / DMT / $AlCl_3$



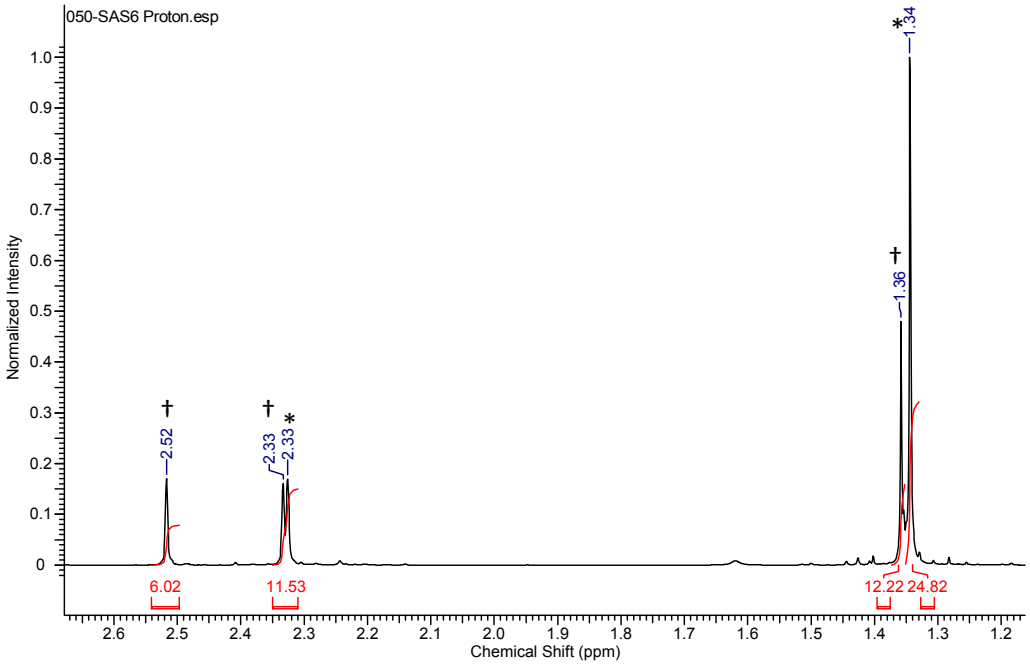
^{11}B NMR Spectrum of in-situ borylation of *m*-xylene after 18 hrs at 140°C with BCl_3 / DMT / $AlCl_3$



^{1}H NMR of the aromatic region of the crude mixture:



^{1}H NMR of the alkyl region of the crude mixture:

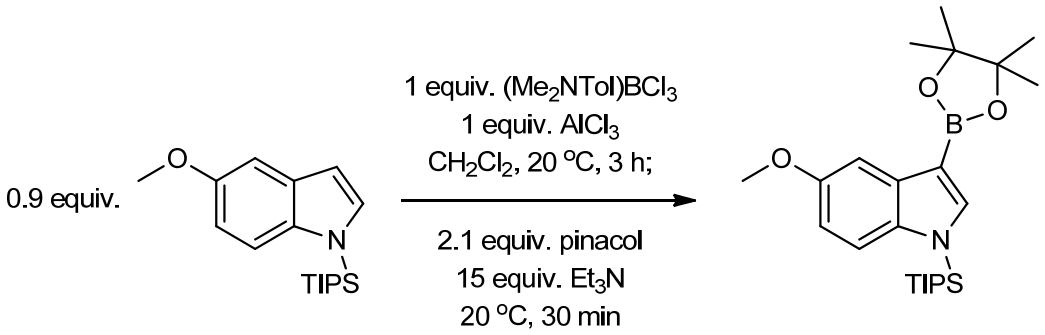


∞ - un-reacted *m*-xylene

† - kinetic product, 1,2,4-borylated *m*-xylene

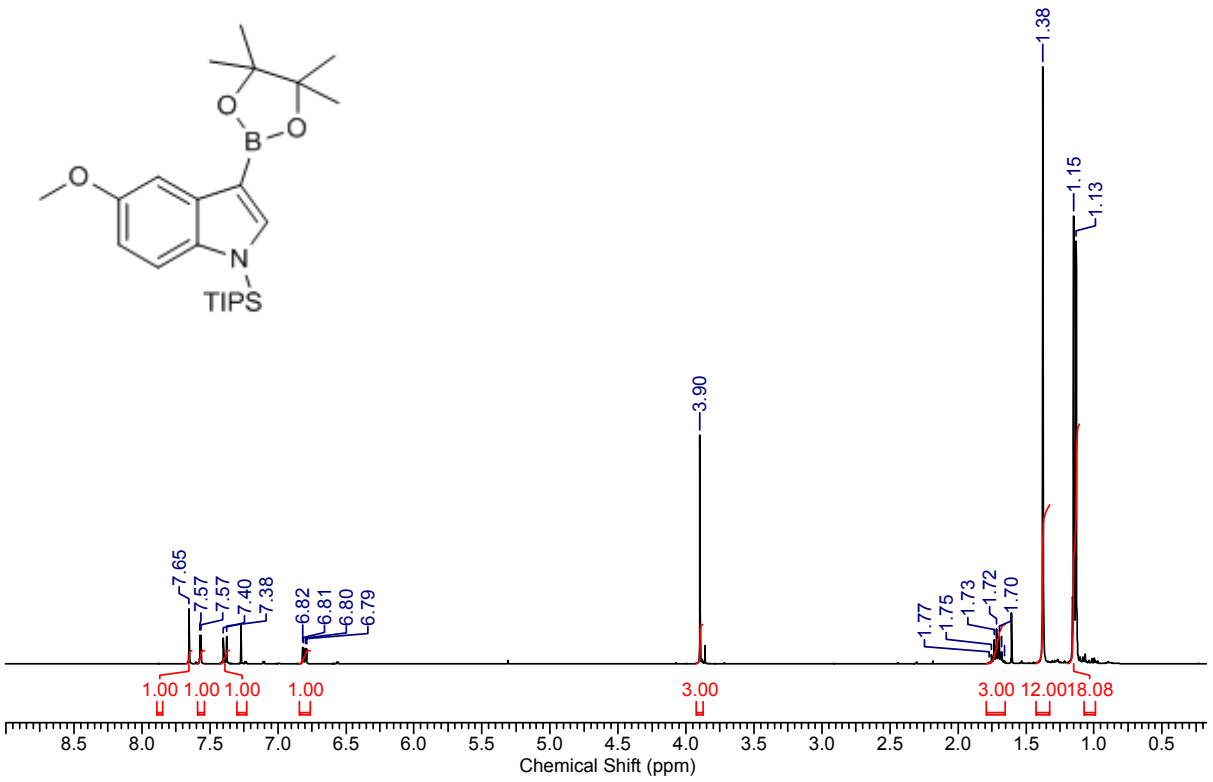
* - thermodynamic product, 1,3,5-borylated *m*-xylene

5-methoxy-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(triisopropylsilyl)- indole, 8m

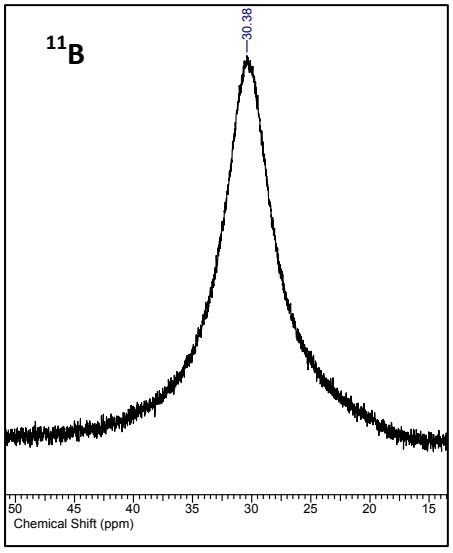


In an oven dried Young's NMR tube under inert atmosphere $Me_2NTol\text{-}BCl_3$ adduct (50 mg, 0.20 mmol, 1 eqiv.) was dissolved in dry CH_2Cl_2 (1 ml) followed by addition of powdered $AlCl_3$ (27 mg, 0.20 mmol). The reaction mixture was agitated until all $AlCl_3$ dissolved and 5-methoxy-1-(triisopropylsilyl)-indole (54 mg, 0.18 mmol, 0.9 equiv.) was added. After agitating the mixture for 3 hours, Et_3N (0.41 ml, 0.94 mmol, 15 equiv.) and pinacol (as solid in one portion) (49 mg, 0.41 mmol, 2.1 equiv.) were added. Caution this is a very exothermic process, on larger scales care must be taken (addition of the reaction mixture to a Et_3N solution of pinacol is recommended). Then, the reaction mixture is poured into a round-bottom flask and the NMR tube washed with CH_2Cl_2 (2 x 1ml). Volatiles were removed under vacuum. The resulting solid was suspended in hexane (30ml) and the solid removed by filtration, upon washing with further hexane (2 x 10 ml). The extracts were combined and the volatiles removed under vacuum to give the crude product which was purified by flash column chromatography on silica gel (eluent hexane : CH_2Cl_2 1 :9 to hexane : CH_2Cl_2 = 2 : 8). The product was dried for 24 h at $1x10^{-2}$ torr to remove residual Me_2NTol giving a white solid (59 mg, 77%).

The NMR data was identical to that previously reported,[1] and representative spectra of the bulk material are shown overpage.

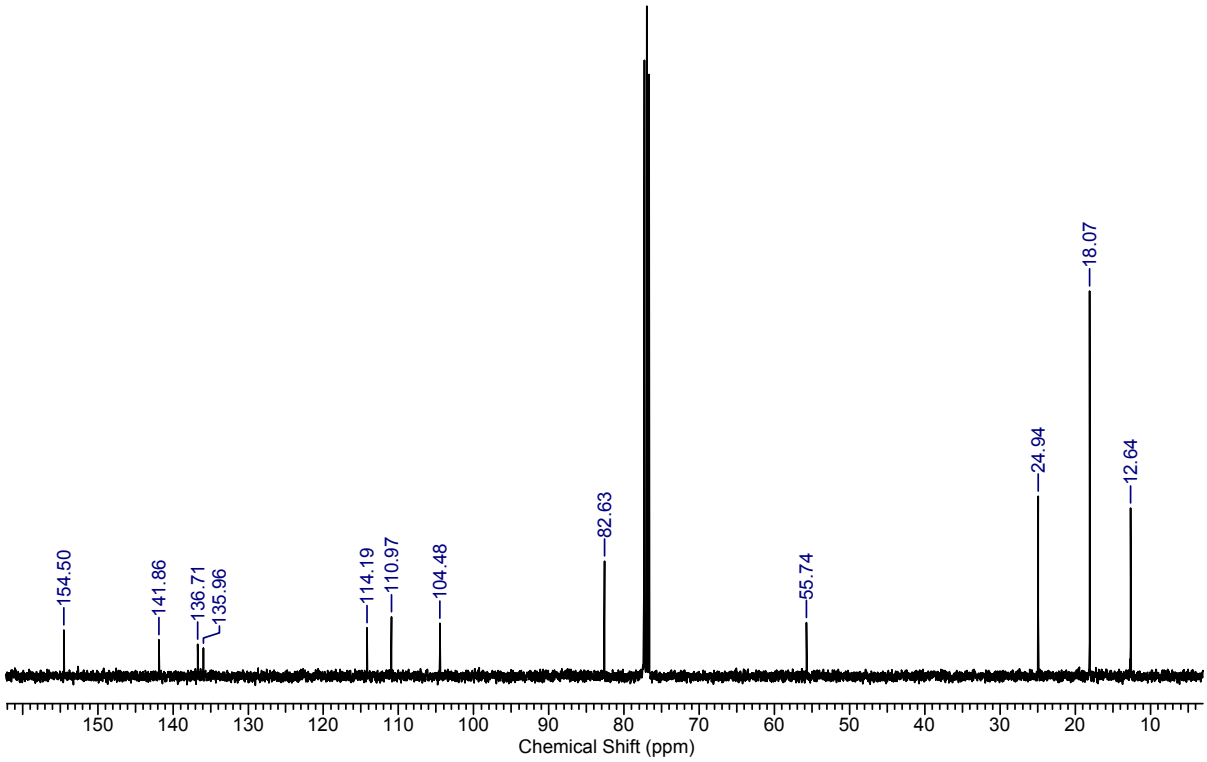

O
B
O
O
N
TIPS
7.65
7.57
7.57
7.40
7.38
6.82
6.81
6.80
6.79
3.90
1.77
1.75
1.73
1.72
1.70
1.38
1.15
1.13
1.00 1.00 1.00 1.00
3.00
3.00 12.00 18.08
Chemical Shift (ppm)

^{1}H

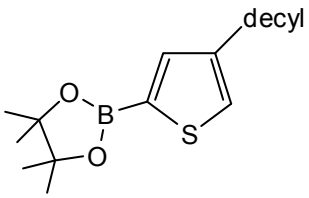

30.38
Chemical Shift (ppm)

^{11}B

$^{13}C\{^{1}H\}$



Preparation of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-decyl-thiophene, **9m**

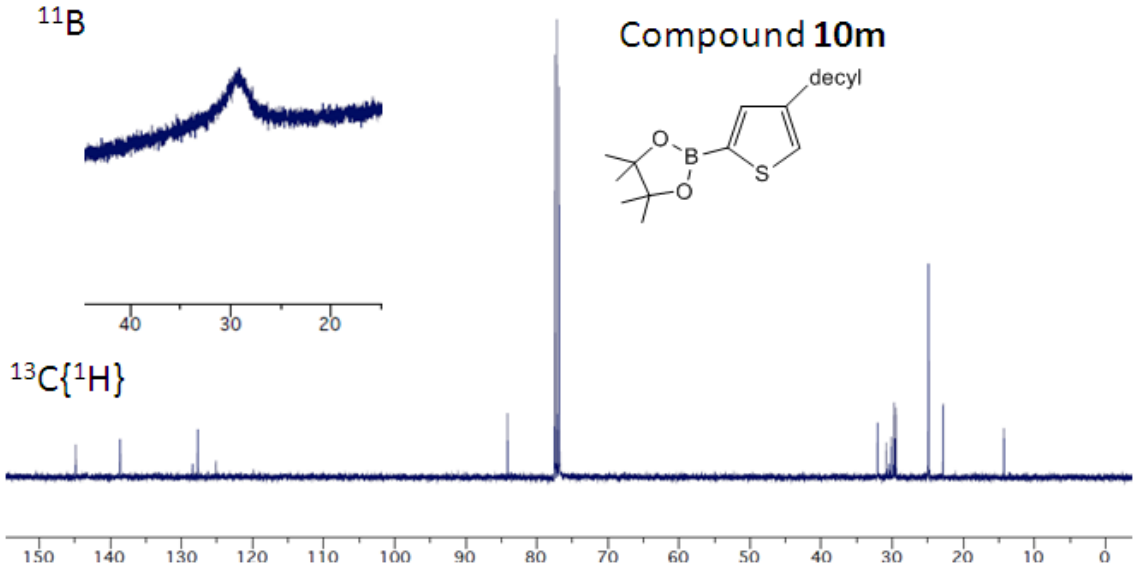


BCl_3 (1M in dichloromethane) (0.22mL, 1.2eq), *N,N*-dimethyl *p*-toluidine (31µL, 1.2eq) and dry dichloromethane (0.2mL) were added by syringe to a J. Youngs NMR tube. In a glovebox, $AlCl_3$ (25mg, 1eq.) and 3-decylthiophene (46mg, 1eq.) were added consecutively. After 10 minutes, the NMR tube was then taken out of the glovebox and rotated for 18h. Then, triethylamine (0.4mL, 15eq) was added followed by addition of pinacol (55mg, 2.5eq). The NMR tube was washed with dichloromethane (2mL) and the resulting mixture was evaporated under vacuum. To the resulting solid, hexane (3mL) was added and the mixture was sonicated for 1 minute. The solids were removed by filtration, upon washing with further hexane (3mL), the extracts were combined and the volatiles removed in vacuum to give the crude product which was purified by flash chromatography through a short plug of neutral alumina using hexane as solvent to give a colourless crystalline solid. Yield: 93%. NMR spectra are closely similar to that reported previously for Pinacol ester of 4-hexylthiophene-2-boronic acid,[7] and representative spectra are shown overpage.

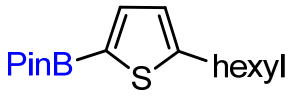
^{1}H-NMR (400 MHz, $CDCl_3$): 7.47 (s, 1H), 7.21 (s, 1H), 2.62 (t, J= 7.7Hz, 2H), 1.61 (m, 2H), 1.34 (s, 12H), 1.25 (m, 14H), 0.88 (m, 3H).

^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$): 144.7, 138.5, 127.5, 84.0, 32.0, 30.8, 30.1, 29.8, 29.7, 29.6, 29.5, 29.4, 24.9, 22.8, 14.3

^{11}B-NMR (128 MHz, $CDCl_3$): 29.1



5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,hexyl-thiophene, **10m**



BCl_3 (1M in dichloromethane) (0.22mL, 1.2eq), *N,N*-dimethyl *p*-toluidine (31µL, 1.2eq) and dry dichloromethane (0.2 mL) were added by syringe to a J. Youngs NMR tube. In a glovebox, $AlCl_3$ (25mg, 1eq.) and 2-hexylthiophene (31mg, 1eq.) were added consecutively. After 10 minutes, the NMR tube was then taken out of the glovebox and shaken for 18 h. Then, triethylamine (0.4mL, 15eq) was added followed by addition of pinacol (55mg, 2.5eq). The NMR tube was washed with dichloromethane (2mL) and the resulting mixture was evaporated under vacuum. To the resulting solid, hexane (3mL) was added and the mixture was sonicated for 1 minute. The solids were removed by filtration, upon washing with further hexane (3mL), the extracts were combined and the volatiles removed in vacuum to give the crude product which was purified by flash chromatography through a short plug of neutral alumina using hexane as solvent to give a colourless crystalline oil. Yield: 67%. The NMR spectra are identical to that reported previously.[8]

1H-NMR (400MHz, $CDCl_3$): 7.46 (d, *J*= 3.4Hz, 1H), 6.86 (dt, *J*= 3.4Hz, *J*= 0.8Hz, 1H), 2.85 (t, *J*= 7.7Hz, 2H), 1.67 (quin, *J*= 7.7Hz, 2H), 1.33 (s, 12H), 1.28 (m, 6H), 0.87 (m, 3H).

13C-NMR (100MHz, $CDCl_3$): 153.8, 137.3, 125.8, 83.8, 31.6, 31.5, 30.1, 28.7, 24.7, 22.5, 14.1.

11B-NMR: 29.1

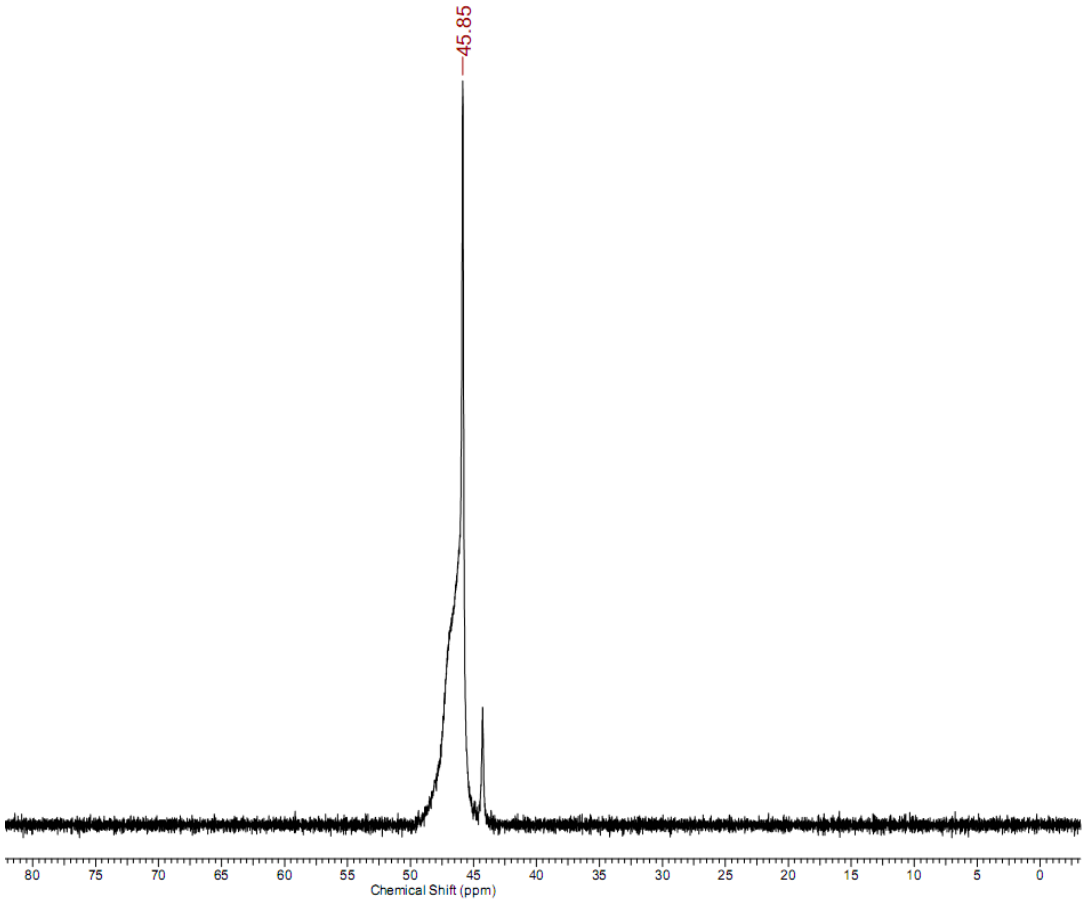
Reaction of BBr_3, Lutidine and $AlBr_3$ in 1,2-dichloroethane

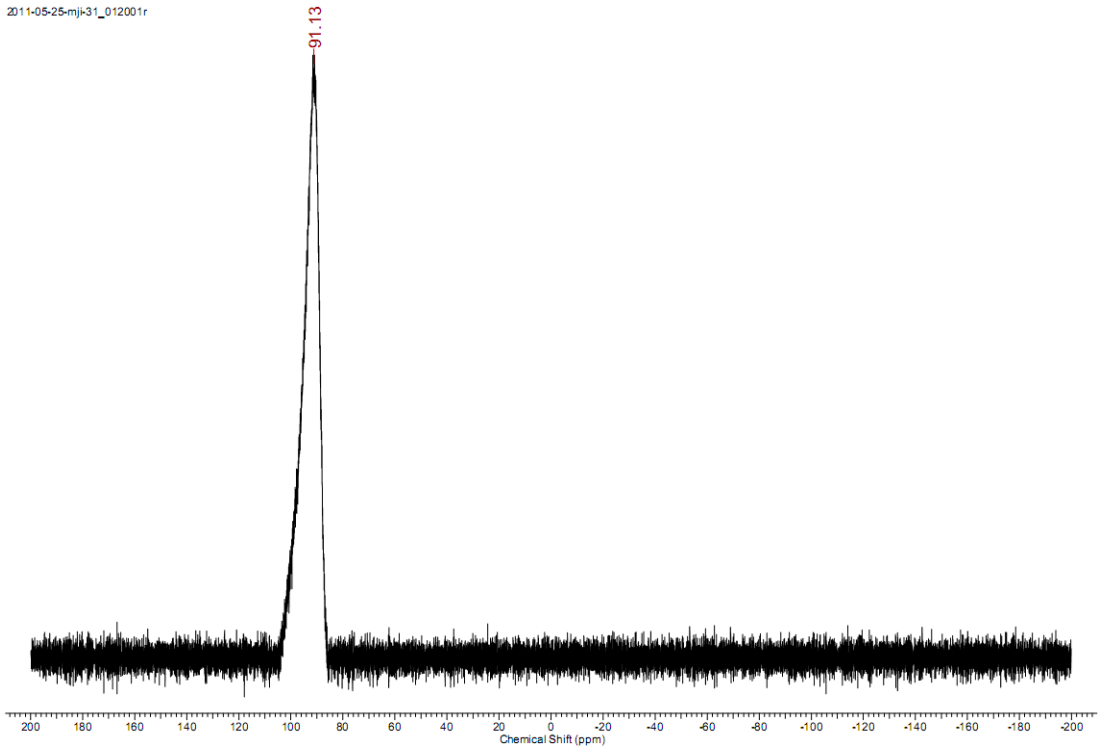
it is noteworthy that attempts to make [(2,6-lutidine)BBr_2][$AlBr_4$] led to rapid activation of 1,2-dichloroethane, and the formation of [(2,6-lutidine)BCl_2]$^+$ [$AlBr_xCl_{4-x}$]$^-$ as the major boron containing products.

In a J. Young's NMR tube containing a sealed capillary filled with $(CD_3)_2SO$, BBr_3 (1.0 M in hexanes, 0.1 ml, 0.10 mmol, 1 equiv.) was slowly added to a solution of 2,6-lutidine (11.5 µl, 0.10 mmol, 1 equiv.) in 1,2-dichloroethane (0.8 ml). Then $AlBr_3$ (27 mg, 0.10 mmol, 1 equiv.) was added and shaken until all $AlBr_3$ dissolved.

The following NMR spectra were obtained (background features containing were subtracted from both the ^{11}B and the ^{27}Al spectra).

^{11}B: The major resonance at +45.9 ppm is attributable to BCl_3, whilst the broad shoulder downfield is due to the borenium cation [2,6-lutidine)BCl_2]$^+$.

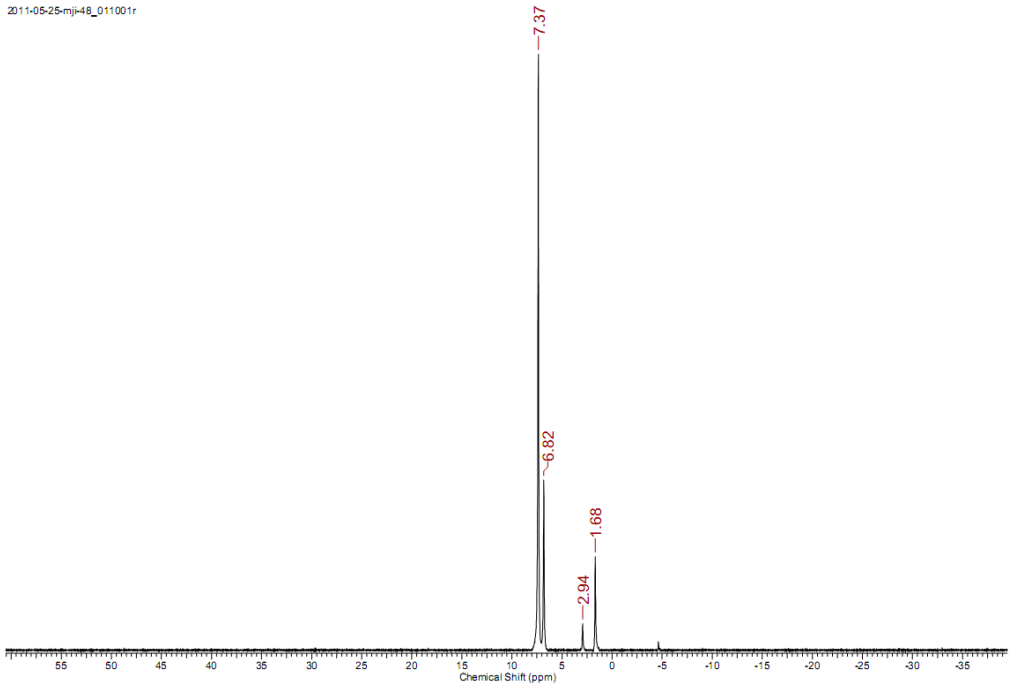


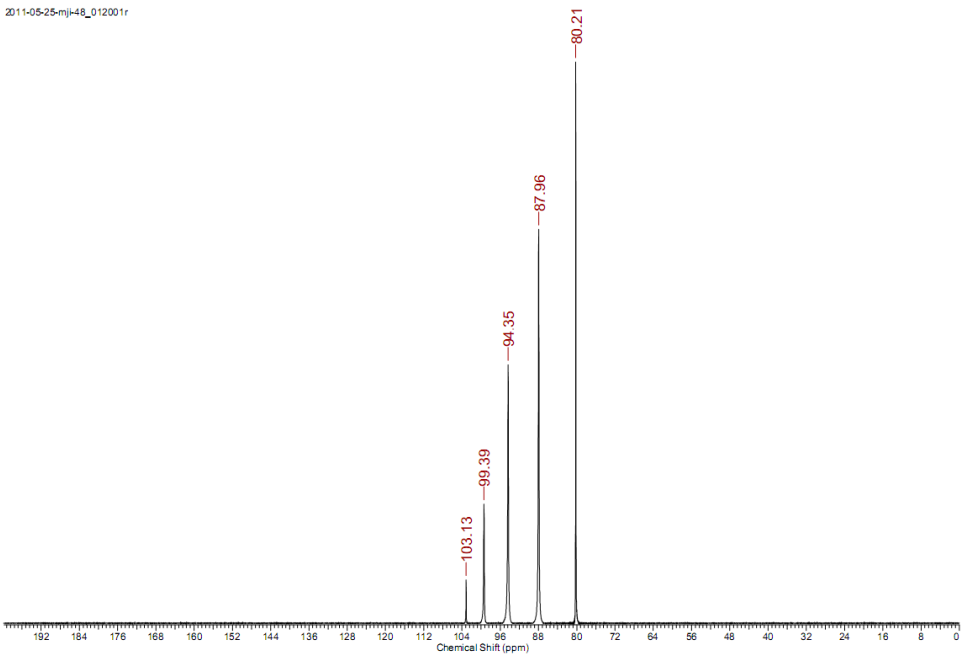


Above the ^{27}Al NMR.

On addition of a second equivalent of 2,6-lutidine the following spectra were obtained.

Below ^{11}B NMR: The peaks at 7.4 and 6.8 ppm are attributable to the 2,6-lutidine→BCl_3 and the boronium cation $[(2,6\text{-lutidine})_2BCl_2]^+$.

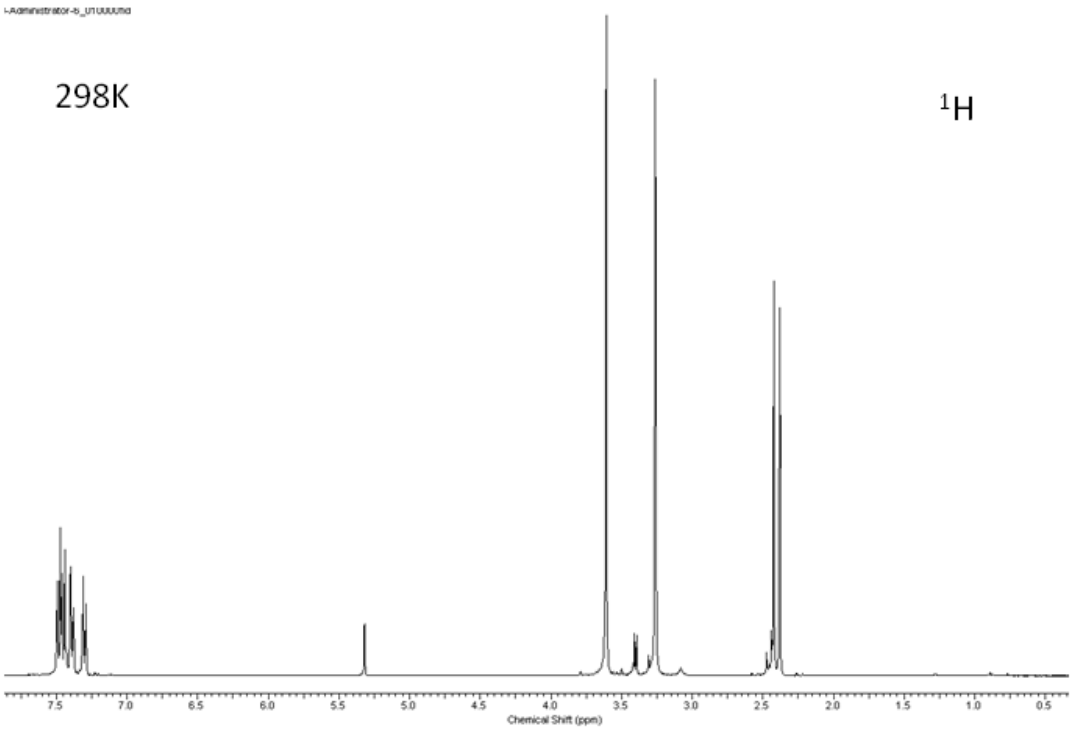


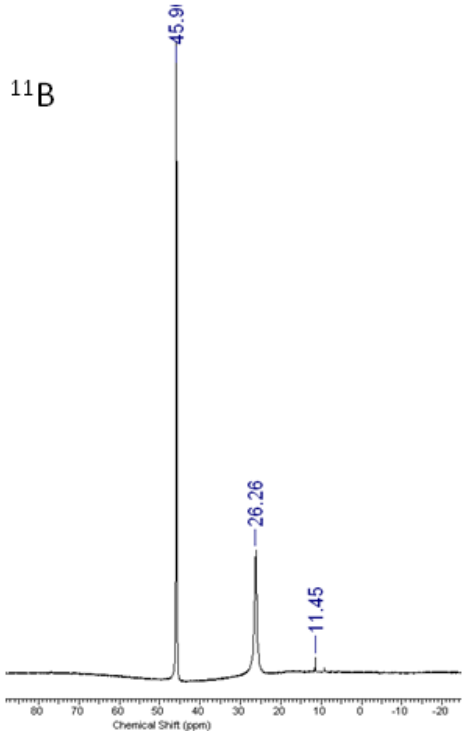


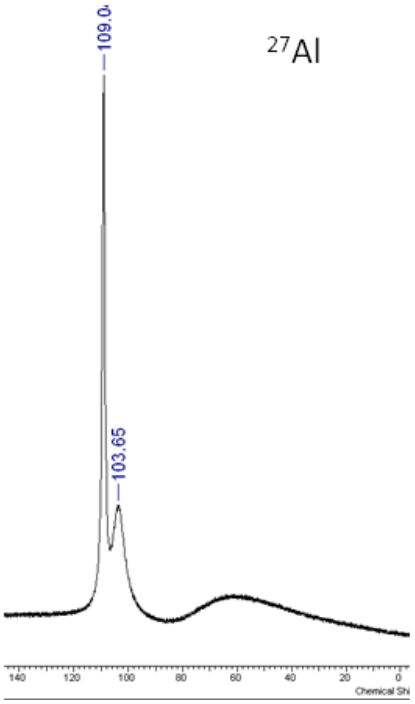
Above the ^{27}Al NMR spectrum showing resonances for $[AlCl_xBr_{4-x}]^-$, X = 0 – 4.

The equimolar combination of $Me_2NTol/BCl_3/AlCl_3$ in CD_2Cl_2

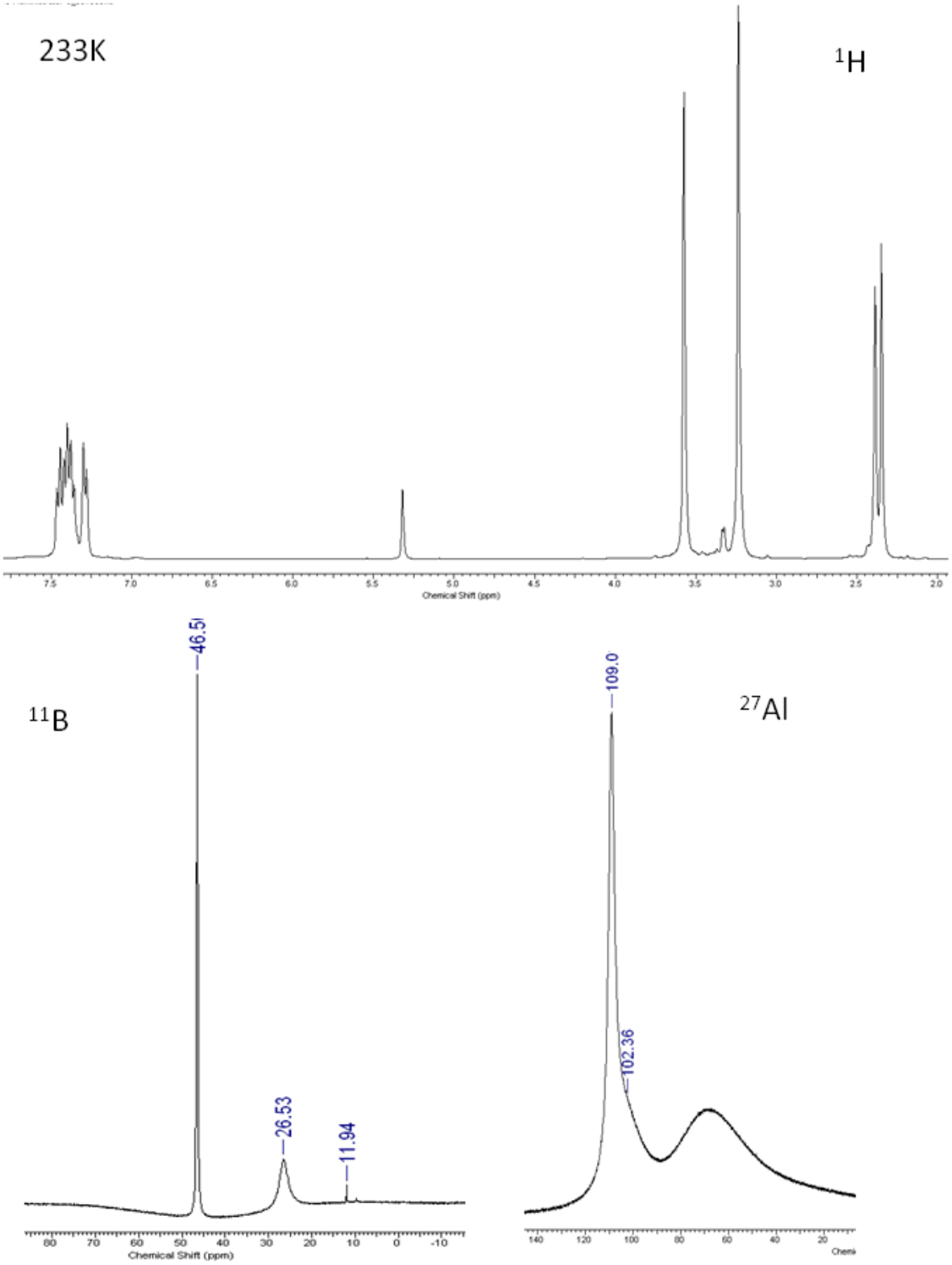
Representative spectrum at 298K of the product from the equimolar combination of $Me_2NTol/BCl_3/AlCl_3$ in CD_2Cl_2 are shown below. The minor peak at 11.5 ppm in the ^{11}B NMR spectrum does not correspond to the neutral adduct Me_2NTol-BCl_3 (this resonates in the ^{11}B NMR spectra at 9.68 ppm by independent synthesis). The resonances at 3.25 in the ^{1}H and at 109.0 in the ^{27}Al spectra , respectively correspond to Me_2NTol-$AlCl_3$.


298K
^{1}H
Chemical Shift (ppm)


^{11}B
45.9
26.26
11.45
Chemical Shift (ppm)


^{27}Al
109.0
103.65

NMR spectra on the equimolar combination of BCl_3 / Me_2NTol / $AlCl_3$ at 233K.



There are no significant changes on cooling to -70ºC beyond broadening of the resonances..

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